UNIVERSAL
LIBRARY

OU_162709

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 541
T58C
Accession No.

Author Timmerman, J.

Title Chemical Species

This book should be returned on or before the date last marked below

CHEMICAL SPECIES

CHEMICAL SPECIES

(LA NOTION D'ESPÈCE EN CHIMIE)

BY

JEAN TIMMERMANS
PROFESSOR OF PHYSICAL CHEMISTRY
UNIVERSITY OF BRUSSELS

TRANSLATED FROM THE
REVISED FRENCH MANUSCRIPT BY

RALPH E. OESPER
PROFESSOR OF ANALYTICAL CHEMISTRY
UNIVERSITY OF CINCINNATI

MACMILLAN AND CO., LIMITED
ST. MARTIN'S STREET, LONDON
1941

PRINTED IN U.S.A.

TRANSLATOR'S PREFACE

Friedrich Richter, editor of Beilstein *Handbuch der organischen Chemie,* in a discussion of the selection of the values of the constants to be included in this authoritative encyclopedia stated,[1] "So far as possible, only the best should be taken from the welter of available physical data.—The principles to be followed in such critical choices have been laid down by Timmermans." Dr. Richter refers here to *La Notion d'Espèce en Chimie,* published at Paris in 1928. Its author has been Director of the International Bureau of Physico-Chemical Standards at Brussels since its creation in 1921, an appointment that was logically dictated by his interest and competence in the field of pure compounds and the determination of their constants.

Unfortunately, probably through lack of proper advertising, this valuable little book became known to too few chemists and has never been accorded the attention it merits. At the translator's request, Professor Timmermans consented to a reissue in English, and kindly made additions and alterations in order to bring the text down to date.

The book is divided into four main parts: Definition of chemical systems; Pure materials; Determination of physical constants; Selection from the literature of the most suitable method of purification, and of the most probable value of the constants of pure materials. The treatment of these topics is neither complete nor exhaustive, but by means of apposite examples it illustrates typical difficulties and solutions of problems that frequently confront every chemist who is interested in the preparation of pure materials and the appraisal of their purity. Both the novice and the seasoned veteran need to be familiar with the chemical doctrines brought together here. The translation has been made to further this acquaintance.

---

[1] **"How Beilstein is made," J. Chem. Education, *15*, 314 (1938).**

Ralph E. Oesper

TABLE OF CONTENTS

Chapter *Page*

I. Introduction 1

PART I

Definition of Chemical Systems

II. Historical Development of the Concept of Chemical Species 6

III. The Criteria of the Phase Rule. 12

IV. Cases Where the Criteria of the Phase Rule Must Be Applied with Discrimination. 18

V. Polymorphism and Isomerism 25

VI. Static and Dynamic Isomers 33

VII. Systems Not in Stable Thermodynamic Equilibrium. . 39

VIII. Objections to Particle or Corpuscular Theories . . . 45

PART II

Pure Materials

IX. History and Definition 57

X. General Methods of Purification 64

XI. Theory of Fractionation 70

XII. Fractional Distillation and Condensation. 76

XIII. Other Physical Methods of Purification 82

XIV. Ordinary Purification Reagents 88

XV. Chemical Criteria of Purity. The Sensitivity of Reagents 92

XVI. Physical Criteria of Purity 99

PART III

Determination of Physical Constants

XVII. The Precise and Accurate Measurement of a Constant . 109

XVIII. Units, Standards and Fixed Points 114

XIX. Approximation of Experimental Measurements . . . 121

XX. The Best Possible Use of Experimental Data . . . 128

Chapter *Page*
XXI. The Theory of Least Squares 134
XXII. Utilization of the Observed Values of a Quantity When the Number of Observations Exceeds the Number of Unknowns 141

PART IV

THE WAY TO FIND IN THE LITERATURE THE BEST METHOD OF PURIFICATION AND THE MOST PROBABLE VALUE OF THE CONSTANTS OF PURE MATERIALS. EXAMPLES AND APPLICATIONS

XXIII. Specialized Laboratories and Studies 151
XXIV. Critical Appraisal and Choice of Published Data . . . 159
XXV. Examples of Pure Materials 166
XXVI. Scientific and Technical Application of Pure Materials . 173

PART I

DEFINITION OF CHEMICAL SYSTEMS

CHAPTER I

INTRODUCTION

OUR senses inform us that our natural surroundings are essentially heterogeneous. In fact, their properties and hence their internal constitution differ according to the objects or the substances which we distinguish in these surroundings. The philosopher asks what is the ultimate reality concealed from us by the variable appearance of things, while the man of science accepts *a priori* the evidence furnished by his senses. His goal is to characterize and to identify with the greatest possible clarity the apparently different substances with which he deals. In this regard the interests of the scientist, who strives to be precise, agree with the needs of practical life, which require exact information of the properties of materials so as to use them as rationally as possible. Knowledge of nature reaches us through our senses; therefore, we always begin to distinguish a given material environment by its effects on our sense organs. However, such characteristics are essentially qualitative and subjective, and so do not lend themselves to the indisputable and precise usage required by science.

In industrial practice materials have come to be defined much more directly by stating the value of this or that particular property in terms of numerical coefficients. Patently this is a great advance, since the barrier separating the domains of mere qualitative knowledge and of definite measurement is thus surmounted. But the numerical statements that content the technologist usually will not satisfy the pure scientist because the numerical coefficients of the former lack both precision and certainty; precision since they are carried to too few significant decimal places, certainty because a given property of a raw material often varies over a rather wide range.

This insufficiency of much of the technical data has two causes:

(a) The physical-chemical constitution of many materials used industrially is not defined with sufficient exactness to eliminate all ambiguity. For instance, oak, depending on its origin, may have very appreciable differences in internal structure and consequently all its properties will show concomitant variations, within rather wide limits, around an average value. The same is true of a stone, of butter, of gasoline, of a rope, etc.

(b) The properties with which the practical man must be familiar are exceedingly complex and depend on a number of factors, as yet not analyzed in detail. For instance, the tractional resistance of a specimen of metal varies not only with the chemical composition of the alloy, but also with the size of the grains, the rate of cooling, the mechanical treatment since its fabrication, its form, the strains to which it was subjected, etc.

So complicated a problem has, up to now, been only approximately solved. The value given to the constant will then frequently vary to a high degree with the method of measurement employed, with time, etc. Difficulties of the same type hamper attempts to measure accurately the yield of a dephlegmator, or to give an exact numerical definition of the color of a material, etc. In all these cases the problem is set with too little exactness to permit a perfectly precise solution.

The man of pure science endeavors to obtain a more faultless result by avoiding these causes of indefiniteness; he has sought to study only such well-defined constants as can be measured with exactitude because all the conditions influencing their value have been exposed. To arrive at the same goal, the physical chemist purposes to give as complete and comprehensive a definition as possible to the different material surroundings, leaving no chance for ambiguity.

Qualitative and quantitative chemical analysis seeks to determine the substances present in a material system and their relative proportions, but usually such examinations do not disclose completely whether the system is homogeneous, nor do they reveal the mutual relations of its different constituents. A specimen of bronze, for instance, contains copper and tin. Analysis alone however cannot reveal whether these two elements are simply juxtaposed in the form of microscopic particles, or whether they form a perfectly homogeneous solid solution, or whether they are combined chemically. For this reason, authors of elementary texts usually deem it indispensable to devote a whole paragraph to the facts which led chemists to the conclusion that the atmosphere is a mixture and not a definite compound of oxygen and nitrogen. Finally, water, considered by the ancients as an element, was shown by the work of Cavendish and Lavoisier to be a compound. But within the last few years the presence, as an impurity, of 1/6000 of heavy water has demonstrated that water is not the ideal pure material, nor the perfect standard, as had been believed. To solve such problems, it is indispensable to use certain principles of physical chemistry, which enable the chemist to interpret correctly the results of analyses, and to classify material systems as elements, compounds, homogeneous solutions and heterogeneous mixtures.

Lavoisier [1] in a frequently quoted passage wrote: "The impossibility of separating the nomenclature of a science from the science itself is owing to this, that every branch of physical science must consist of three things: the series of facts which are the objects of the science, the ideas which represent these facts, and the words by which these ideas are expressed. Like three impressions of the same seal, the word ought to produce the idea, and the idea to be a picture of the fact. And, as ideas are preserved and communicated by means of words, it necessarily follows that we cannot improve the language of any science, without at the same time improving the science itself; neither can we, on the other hand, improve a science without improving the language or nomenclature which belongs to it. However certain the facts of any science may be, and however just the ideas we may have formed of these facts, we can only communicate false impressions to others, while we want words by which these may be properly expressed."

There is no domain where this clarity of definition and this precision of terms is more necessary to the progress of chemistry than in the present one, which deals with the distinction between the various types of materials. This book will comprise an examination of the most favorable conditions for the determination of a physical chemical constant. The discussion will naturally fall into four parts to answer the following questions:

---

[1] Lavoisier, Elements of Chemistry, translated by Robert Kerr, Preface, p. XIV, Edinburgh (1790).

I. How may a given physical-chemical system be defined without ambiguity? This is the problem of chemical species.

II. How may such a system be realized? This is the problem of pure materials.

III. How may its constants be measured with precision and exactitude?

IV. How may the best method of purification and the most probable value of the constants of pure materials be found in the literature?

CHAPTER II

HISTORICAL DEVELOPMENT OF THE CONCEPT OF CHEMICAL SPECIES

THE concept of species plays just as important a role in chemistry as it does in the biological sciences. The study of its historical development will show the great influence which it exerted in the formation of the present ideas of the internal constitution of the material world.

Before Lavoisier, many of the chemical ideas were not clearly defined, particularly in the domain with which this book is concerned. The case of mercuric oxide is a classic example. It had long been known that this substance if heated in close contact with charcoal produced metallic mercury. According to Stahl, the champion of the phlogistic theory that was generally accepted about 1750, the material now called mercuric oxide was a "calx" and considered as an element. On heating the mixture, the charcoal, rich in combustible fluid or "phlogiston," gave up a part of this to the "calx" and transformed it into a phlogisticated compound, mercury.

Lavoisier made this interpretation of the phenomenon untenable by showing that the quantity of mercury obtained by heating a given weight of the mercury "calx" weighed *less* than the parent substance; if heated in the absence of charcoal, the calx liberated a gas, oxygen, whose weight exactly equaled the difference between that of the original oxide and of the mercury obtained. In the face of these facts, it was evidently more logical to consider mercuric oxide as a compound formed by the union of two simpler substances, oxygen and mercury; the elementary "calx" of Stahl became a compound, his "phlogisticated" mercury a simple substance.

As a result of his studies (1781) on mercury, lead, tin, sulfur, phosphorus, carbon, etc., Lavoisier clearly specified the difference between elements and compounds. He wrote:[1]

"I shall therefore only add upon this subject, that if, by the term *element*, we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable we know nothing about them; but if we apply the term *element* or *principle* of *bodies* to express our idea of the *last point of which analysis is capable of reaching*, we must admit, as elements, all the substances into which we are not able, by any means, to reduce bodies by decomposition." This is a striking example of the importance of results obtained with the aid of quantitative measurements, when these are interpreted by a scientific mind capable of comprehending their complete significance.

Twenty years later (1801–1803), the difference between *definite compounds* and *mixtures* was elucidated by a dispute between Berthollet and Proust.[2] The former contended that there is no fundamental difference between compounds and solutions. Solutions are "indefinite" compounds, whose composition varies with the conditions; compounds possess a definite composition only as the result of the effects of secondary causes (such as saturation of the medium in which they are formed) which limit the range of their variation.

---

[1] Lavoisier, *op. cit.*, p. XXIV.

[2] Berthollet, *Essai de Statique Chimique*, Paris (1803). Proust, Ann. chim. phys., [1] *32*, 31, 45 (1800).

Proust defended the law of definite proportions, promulgated previously by Dalton in support of the atomic theory, by citing the experiments and analyses of Richter and of Wenzel (1740–1793). To these findings he added the results of his own experimental studies which showed that the compounds obtained under very different conditions (temperature, concentration, method of preparation) always have an identical quantitative composition, or that this varies only by abrupt steps, so as to produce two or more distinctly different compounds (maximum and minimum compounds) and no intermediate ones. This demonstration of the correctness of the laws of definite proportions and of multiple proportions gave him the criterion used ever since to distinguish *solutions* from true *compounds*.

There remains a large class of systems of variable composition, *mixtures*, which, in reality, include quite different types. The result of the slow and often imperceptible progress of the exact sciences in the second half of the nineteenth century has been to delineate the domain of solutions. To solutions have been opposed, on the one hand, more or less unstable *addition compounds* (such as hydrates) and on the other, heterogeneous *aggregates*, whose constituents are simply juxtaposed to form a rather coarse mixture.

Two remarkable cases have played an important role in the evolution of modern ideas of the inner constitution of mixtures. The first is that of the liquid hydrates of strong acids, studied by Roscoe (1859). If the incipient boiling temperatures of various mixtures of nitric acid and water are determined, it is found that this temperature is a maximum for one of the mixtures. This particular (so-called azeotropic) mixture distils unchanged, and it may be collected as the last fraction of the distillate from solutions of any concentration. Roscoe and Dittmar[1] showed that, despite its unchanging composition, this mixture is not a true compound; actually, its concentration varies with the pressure under which the distillation is made. The azeotropic mixture contains the following percentages of nitric acid, if distilled under the given pressures: 66.7 (70 mm.); 67.6 (150); 68 (760); 68.6 (1220).

This variation of the concentration of the azeotropic mixture removes all doubts; it is not a definite compound. The true hydrate, existing in solutions of nitric acid in water, was isolated by *crystallization* of concentrated solutions;[2] its composition remains exactly equimolecular over the whole range of temperatures and pressures at which the crystalline state exists.

Analogous observations have been made since on many other addition compounds (*solvates*). They constitute well-defined chemical species in the solid state, but they partially dissociate on going over to the liquid state, producing solutions containing the compound along with its constituents.

The foregoing example allowed the setting of the exact boundary which separates *solutions* from *addition compounds*. The *solutions* were definitely separated from the *aggregates* by Guthrie's *cryohydrates*.[3] If a solution of 30.7 gm. of sodium chloride in 100 gm. of water is cooled, it remains liquid down to −21.3°, then it entirely solidifies at a constant temperature. Throughout this crystallization the solid and the liquid phase have identical compositions, so that a solution of this kind, at first sight, seems to have all the characteristics of a definite hydrate. This is not the case. Microscopic examination reveals a confused mass of crystals of salt and of ice, side by side. If the freezing is carried out under varying pressures, the composition of the cryohydrate varies slowly, to be sure, but continuously.

---

[1] Roscoe and Dittmar, Ann., *112*, 327 (1859).

[2] Küster and Kremann, Zeit. anorg. allgem. Chem., *41*, 21 (1904).

[3] Guthrie, Phil. Mag., [4] *49*, 1 (1875).

A cryohydric solution then does not differ essentially from solutions of other concentrations; like the latter, it produces, on freezing, a crystalline *conglomerate* and not a definite compound.

A solution, namely a homogeneous system of variable concentration, is thus differentiated from a definite compound which possesses an invariable composition and from a heterogeneous conglomerate. The subsequent development of physical chemistry has given this idea a more and more extended field of application. Limited at first to liquid mixtures, the term solution has been applied equally to mixtures of gases and finally to solid solutions. As early as 1866, Lecocq de Boisbaudran [1] in a note, which unfortunately was not published until 1890, stated to the Paris Academy of Sciences: "I do not hesitate to attribute to the same cause, that is, to something approximating isomorphism, the following phenomena:

1. The solution of *certain solids* in each other (Mitscherlich's isomorphism);
2. The solution of *many liquids* in each other;
3. The solution of *all vapors* in each other."

van't Hoff [2] brought about the acceptance of this extension of the idea of solution by his well-known paper on solid solutions. In this, he showed that the *mixed crystals* or *isomorphic mixtures*, formed by the syncrystallization of two or more materials, obey the thermodynamic laws of solutions and ought to be distinguished rigorously from simple aggregates.

---

[1] Lecocq de Boisbaudran, Compt. rend., *113*, 832 (1891): *142*, 196 (1906).

[2] van't Hoff, Z. physik. Chem., *5*, 322 (1890).

These latter systems are easy to recognize. Composed of juxtaposed particles, often microscopic, they may be resolved easily into their constituents by relatively coarse methods, such as the use of heavy liquids to separate materials of different densities, by means of the ultramicroscope that renders visible the particles in colloidal suspensions, etc. The study of *aggregates* (emulsions, conglomerates, colloids, smokes, etc.) often goes beyond the bounds of physical chemistry; the complete definition of these systems requires a consideration of their structure. This is rather the task of the naturalist (anatomist, petrographer) or of the technician (metallographer, etc.). Such was, in broad outline, the evolution which led contemporary physical chemists to define, without ambiguity, the three realizable types of homogeneous phases: elements, compounds, solutions.

The problem of species in chemistry, viewed in this way, is therefore very vast. Its importance is all the greater because the chemical literature is filled with errors such as the description of alleged new compounds which in reality are only mixtures, the confusion of similar compounds, etc. The situation was succinctly stated by Le Chatelier:[1] "The inorganic chemists less favored (than their organic brethren) have too often allowed themselves to be seduced into artificially augmenting the number of real compounds. If we go through the large general treatises on chemistry we can boldly state that at least half of the compounds described there have never existed."

---

[1] Le Chatelier, *Leçons sur le Carbone, le combustion, les lois chimiques*, Preface. Paris (1908).

CHAPTER III

THE CRITERIA OF THE PHASE RULE

THE concepts of element, compound and solution, whose historical development and progressive differentiation have just been reviewed, received exact definitions in the *phase rule* of Willard Gibbs. This rule is based on thermodynamics; the results to which it leads acquire much greater significance from their certainty and the extent of their field of application. The persevering efforts of Wald [1] are largely responsible for the acceptance of this viewpoint, and it definitely acquired the right to be included in the exact sciences after its masterly discussion by Ostwald in his Faraday Lecture of 1904.[2]

Every homogeneous chemical system, with uniform properties throughout, constitutes a phase. A bubble of air, a piece of sugar, a drop of salt water, a fragment of glass, are phases.

A system made up of several phases lying side by side is a *polyphasic aggregate*. A single phase may be scattered in separate islets, but having identical composition and physical chemical constants. Milk, for example, is an emulsion of fat globules suspended in an aqueous solution; two distinct phases, and only two.

A phase can exist only between certain limits of temperature and pressure. If these limits are exceeded the phase goes over into another. For example, water cooled below 0° changes into ice. However, a transformation of this kind can proceed in two different ways. The composition of the two phases undergoing change may remain invariant during the entire course of the phenomenon, or the composition of at least one of them undergoes gradual change. In the first case we are dealing with a *hylotropic* phase, in the second, with a solution. For instance, a dilute salt solution, on cooling, deposits pure ice, while the liquid phase becomes richer and richer in dissolved salt.

---

[1] Wald, Z. physik. Chem., *22*, 253 (1897) ff.

[2] Ostwald, J. Chem. Soc., *85*, 506 (1904).

A hylotropic phase ($\upsilon\lambda\eta$ = residue) may itself be a solution or a pure material. To differentiate these, the transformation which leads to the isolation of the hylotropic phase is repeated at a slightly different temperature and pressure; under these new conditions the hylotropic phase may behave like an ordinary solution. It then is a *hylotropic solution* capable, according to the law of Gibbs-Konovalow, of changing into another phase of the same composition. But this phenomenon can be observed at only one temperature and one pressure, both well-defined, because the composition of this hylotropic

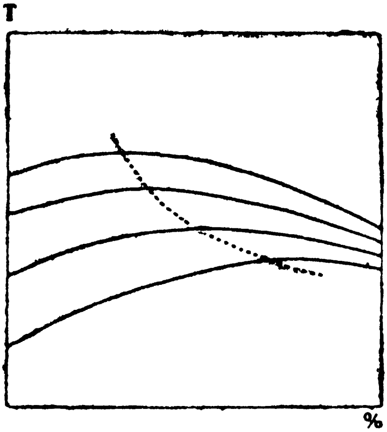


FIG. 1. Variation of the composition of a hylotropic solution with temperature.

solution changes with the temperature and pressure (Fig. 1). An excellent example is furnished by the mixtures of nitric acid and water studied by Roscoe.

If a hylotropic phase can exist, without change of concentration, over an entire range of temperatures and pressures, it is a pure substance, stable within more or less extended limits. If these are exceeded, the substance usually decomposes and again produces a solution (Fig. 2). It thus shows itself to be a *definite compound.*

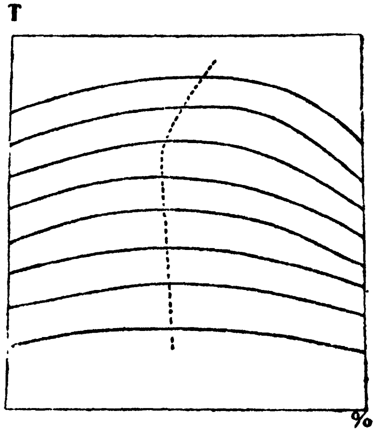


FIG. 2. Constance of composition (in a limited temperature range) of a hylotropic phase corresponding to a definite compound.

Figures 1 and 2 represent the variations of a characteristic property as a function of concentration: the boiling point, for example, measured at a series of pressures, p_1, p_2, p_3, etc. The maximum of each curve corresponds to a hylotropic phase. In Fig. 1 the hylotropic phase is a solution, since its concentration varies with the prevailing pressure. The hylotropic phase in Fig. 2 is a definite compound at the pressures $p_1 - p_4$, under which its concentration does not vary, but it becomes a solution at p_5. Water behaves like a hylotropic phase at not too high temperatures, but above 500° it dissociates partially and its two gaseous constituents can be separated. Therefore, water is a *definite compound* under ordinary conditions, but at high temperatures changes into a *mixture.*

A material which behaves as a hylotropic phase under all attainable temperatures and pressures is an *element.* For instance, neither melting nor boiling changes the composition of copper, nor can it be divided into different materials by fractionation.

To sum up, the phase rule gives a precise distinction between:

aggregates, polyphasic systems;

solutions, whose composition varies continuously during fractionation;

definite compounds, hylotropic phases between certain limits of temperature and of pressure;

elements, hylotropic under all circumstances.

It may be seen then, that one of the most delicate points raised by these definitions is the fundamental distinction between hylotropic phases that are solutions, and those corresponding to definite compounds. In principle, the method of solving this difficulty is to vary the conditions of temperature and pressure of the polyphasic equilibrium to determine whether, under such circumstances, the composition of a hylotropic system remains variable or invariable.

When dealing with an equilibrium involving a vapor phase, changes of pressure result in a rapid alteration of the hylotropic composition. Roscoe showed this in his study of the azeotrope of aqueous solutions of nitric acid. But if only condensed phases are present, the change in the composition of the hylotropic solution is very much slower, and sometimes can be detected only by changes in pressure of several hundred kilograms per square centimeter. Eutectics, notably, behave in this manner.

Another curious problem which raises difficulties of the same kind was encountered by McBain [1] in his study of water solutions of certain soaps (Fig. 3). Within a certain temperature range above the region of crystallization, these systems exhibit the properties of anistropic liquids and become isotropic only when heated more strongly. If the temperatures at which one of these liquid forms passes into the other are plotted as functions of concentrations,

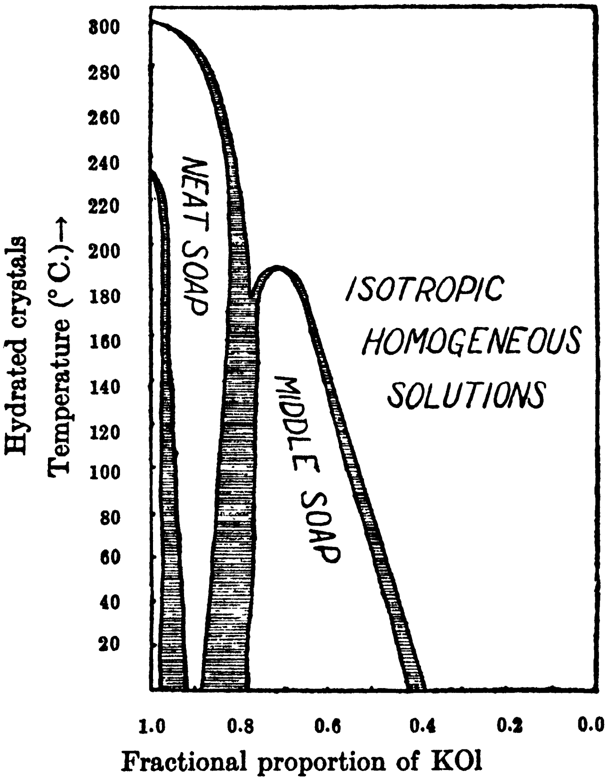


Fig. 3. Equilibria between isotropic solutions and anisotropic systems in the system: potassium oleate plus water.

---

[1] McBain and Elford, J. Chem. Soc., *129*, 421 (1926).

the curve, in certain cases, has a maximum which does not correspond to any simple stoichiometric ratio. This hylotropic system, at this point, can no longer be a definite compound, but is a simple hylotropic solution. To prove this, it will be necessary to demonstrate, for example, a slow change of the hylotropic concentration on repetition of the experiment under higher and higher pressures.

CHAPTER IV

CASES WHERE THE CRITERIA OF THE PHASE RULE MUST BE APPLIED WITH DISCRIMINATION

THE application of these clear definitions sometimes presents difficulties. An historic example is the study of the mixtures of optical antipodes, whose interpretation perplexed even van't Hoff.[1] When they crystallize, these mixtures may produce three types of systems:

(a) A *racemate* (Fig. 4). This contains an equal number of molecules of each of the optical isomers and exhibits all the characteristics of a definite compound. Its compo-

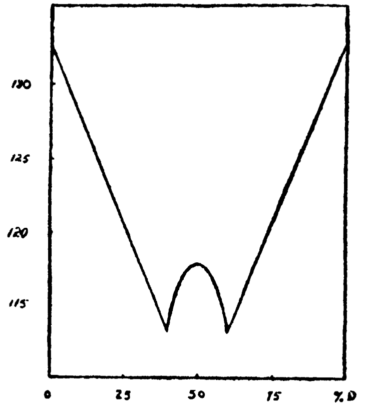


FIG. 4. Freezing-point curve for the system *d*-phenylglycollic acid plus *l*-phenylglycollic acid.

---

[1] van't Hoff, Chem. Ztg., *26*, 1172 (1902); Byk, Z. physik. chem., *45*, 465 (1903).

sition does not change when it is partially dissolved at different temperatures in various solvents. For instance, the two phenylglycollic acids form a racemate that melts at 118°, while the components melt at 133°. The freezing curves intersect in two eutectics symmetrically placed.

(b) A *pseudo-racemate* (Fig. 5). This gives a continuous series of mixed crystals with the two antipodes. The pseudo-racemate is a compound quite like a true racemate. Some writers, rather illogically, prefer to consider the pseudo-racemate as a hylotropic solution, whose concentration remains constant solely because of the symmetry resulting from the identity of the properties of the two antipodes. An example is the carvoximes which melt at 72°, while their pseudo-racemate melts at 92°.

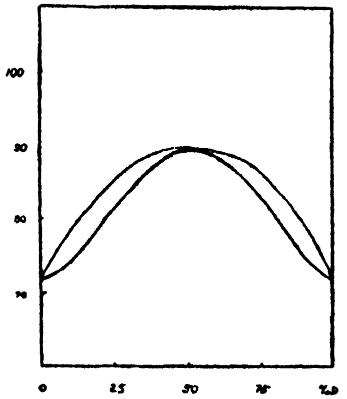


Fig. 5. Freezing-point curve for the system: *d*-carvoxime plus *l*-carvoxime.

(c) A *continuous series of mixed crystals* (Fig. 6). All the constants, except the rotatory power, of these crystals are identical and coincide with those of the pure constituents. A system of this kind, therefore, is a mixture which when melted behaves, at all concentrations, as a definite compound.

How can this difficulty be solved? The phase rule characterizes substances only by their thermodynamic constants, and does not differentiate between two substances whose optical properties alone are opposed to each other. In such a case, thermodynamically speaking, there is present only one component, always identical with itself, whatever the value of its rotatory power. The mixture of the two camphor oximes (m.p. 119°) fulfills these conditions. From the thermodynamic point of view, this mixture behaves like a single substance, even though the rotatory power varies with the concentration of the liquid. This case is analogous to the mixtures of right- and left-handed crystals of quartz or sodium chlorate. Their rotatory power is limited to the crystalline state, and they are treated as a single component from the viewpoint of the phase rule.

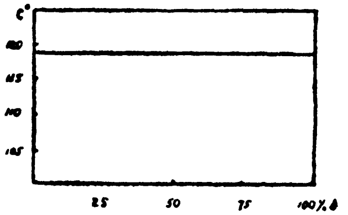


FIG. 6. Freezing-point curve for the system: *d*-camphoroxime plus *l*-camphoroxime.

For many years chemists devoted themselves almost entirely to the study of definite compounds. But as Perrin states in the preface to his excellent book, *Les Principes:* [1] "the progress of physical chemistry has brought the study of solutions to the fore." In a communication to the first Congress of Russian Scientists, held at Leningrad in 1914,

---

[1] Perrin, *Traité de chemie physique. Les Principes,* Paris (1903).

Kurnakow[1] stressed the importance of the following points:

Alloys, rocks, and many other mixtures have regions of solid solutions whose properties differ entirely from those

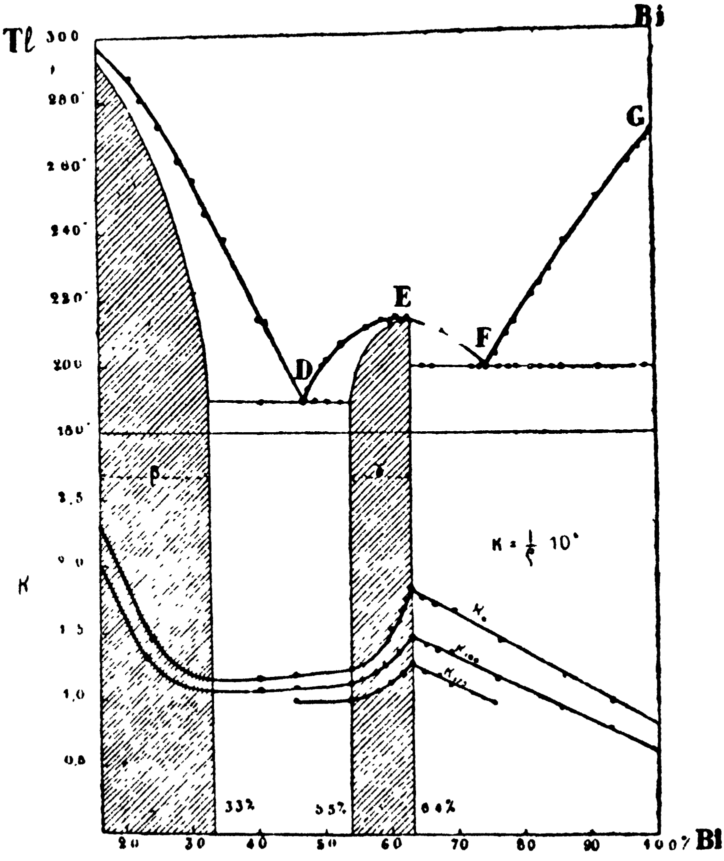


FIG. 7. Freezing-point curve for the system: Thallium plus Bismuth; and curves showing specific conductance of thallium-bismuth alloys at various temperatures.

of the components, although the presence of a definite compound, and especially its exact composition, cannot be demonstrated irrefutably. Zeolites, those natural silicates whose degree of hydration may vary within wide limits without the crystallographic constants being affected, are the classic example of such systems but many others may be cited. The alkaline tellurates, aluminum oxalate, etc., likewise give poorly-defined combinations with water, carbon bisulfide, alcohol and many other organic substances, with mercury, etc., and thus produce veritable absorption compounds.

---

[1] Kurnakow, Z. anorg. allgem. Chem., *88*, 109 (1914).

The alloys of bismuth and thallium, in the concentrations between 57–65% Bi, likewise exhibit remarkable peculiarities that suggest the existence of a definite compound, whose formula cannot be established (Fig. 7). For instance, the maximum of the freezing curve does not correspond exactly to the maximum of the curve of the specific electrical conductivities. Guertler and Schulze [1] have pointed out an analogous case in the alloys of lead with thallium, etc.

In all similar cases, the difficulty arises from the fact that the quantitative composition of the system corresponding to a definite compound is not marked by any peculiarity in the diagram of the polyphasic equilibria. Sometimes the maximum of the melting points of mixed crystals does not correspond to any simple stoichiometric ratio. It occasionally happens that the striking points of phase diagrams do not correspond quantitatively to those furnished by the study of other physical constants of the system, such as the electrical conductivity of the alloy, or its hardness.

An analogous example was discussed in detail by Clendinnen and Rivett.[2] The system, $NH_4Cl + MnCl_2$, studied from the viewpoint of its solubility in water, produces a continuous series of mixed crystals on both sides of the compound $2NH_4Cl \cdot MnCl_2 \cdot 2H_2O$, which was supposed to have been identified from the start. However, this composition of the mixed crystal does not correspond exactly to a minimum of the solubility isotherm and so there is no substantial reason for attributing this precise formula to the compound being sought. Yet, it seems indispensable to admit the existence of such a compound, which alone is capable of forming mixed crystals with ammonium chloride on the one hand, and with hydrated manganous chloride on the other. Without this assumption, it is impossible to see why there are two distinct gaps in the series of mixed crystals, one on each side of this hypothetical compound (Fig. 8).

---

[1] Guertler and Schulze, Z. physik. Chem., *104*, 269 (1923).

[2] Clendinnen and Rivett, J. Chem. Soc., *119*, 1329 (1921).

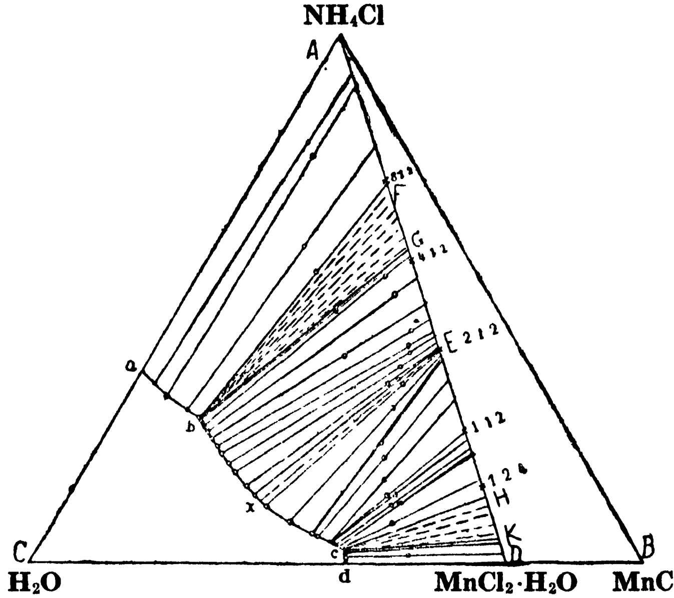


Fig. 8. Triangular phase-diagram of the system $MnCl_2$ plus NH_4Cl plus H_2O at 60°.

In view of such anomalies, whose number increases with the precision and the extent of the studies being made, Kurnakow proposed that the existence of compounds of variable composition be accepted. He calls these *berthollides*, in opposition to the really definite compounds, the *daltonides*. So by a curious reversion to earlier theoretical ideas, the apparently incompatible contradictory conceptions of Proust and of Berthollet are brought side by side, in an ensemble harmoniously including both.

CHAPTER V

POLYMORPHISM AND ISOMERISM

A. *Identical and different specimens*

If compounds are studied from the standpoint of their quantitative composition it soon becomes apparent that materials of identical composition may often appear with quite varied aspects. There are three possible explanations for these differences: the specimens are isomers, polymers, or they differ only externally.

The last case is encountered especially with solids where superficial disturbing causes frequently mask the real identity of the several samples. To test this possibility, the specimens should be subjected to analogous treatment, and then examined to determine whether they still show the same properties. This method is applied whenever it is necessary to discover whether natural products of different origin are identical. For instance, Haller [1] showed that samples of camphor from a variety of sources differed merely in their external appearance. He proved this by purifying them, and then determined their rotatory power and melting point.

The choice of the constant which is to serve in distinguishing similar materials is very important. It ought to lend itself to measurements sufficiently sensitive to reveal minimum differences, and yet its determination should be relatively easy and rapid. The melting point, whose use in the examination of organic compounds was introduced by Liebig,[1] meets these requirements very well. Several milligrams suffice for its approximate determination in a capillary tube. It should be noted, however, that the melting point is not reliable when applied to unstable compounds which decompose instead of melting; they may give quite different melting points, with different rates of heating. For instance, Henry reported the melting point of diisobutyl acetamide to be 100° while Meerburg gave 169°.

---

[1] Haller, Ann. chim. phys., [6] *27*, 392 (1892).

Such errors can be avoided by using the method of instantaneous fusion. Several milligrams of the sample are introduced into very narrow capillaries that are then sealed. Each tube is suddenly plunged into a bath of known temperature, and the true melting point is taken to be the temperature at which complete fusion, observed with a magnifying glass, occurs within a few seconds. This maximum temperature is the limiting value obtained when the time of fusion tends to become so short that the decomposition has not time enough to progress sufficiently to produce a manifest lowering of the melting point.

If two samples show but little difference in their properties it is hard to decide whether they are identical or not. Observers have often been deceived by traces of impurities that were difficult to remove, and have reported samples to be two materials, when in reality there was only one but in varying degrees of purity. This error can best be avoided by continuing the purification of each sample until the property being measured shows a constant value.

---

[1] Liebig [Ann., *3*, 270 (1832)] used a melting point with no comment, so this practice probably is of an earlier date, but the writer has not been able to find an antecedent reference.

Sometimes differences in surface tension make identical materials appear different. The mercuric oxides studied by Hulett [1] are the classic example. If prepared by a dry method, the product consists of red grains, while a wet method results in an impalpable bright yellow powder. This difference in appearance is due solely to the size of the grains, because when the red oxide is ground, it gradually passes, by insensible transitions, through orange to yellow. Surface tension increases with the surface and always tends toward a minimum value; this favors the formation of larger grains at the expense of the smaller ones. Therefore, at room temperature, the yellow oxide is less stable and more soluble (150 mg./liter) than the red (50 mg./liter).

Finally there are some solids whose viscosity at the ordinary temperature is so great that they attain equilibrium with their surroundings only with a provoking slowness. If they are subjected to extreme temperatures or pressures and then returned to ordinary conditions, they retain for a long time the constants corresponding to the conditions to which they were exposed. This is a true hysteresis which leads to a lack of precision and to a peculiar variability in the constants of many metals. For instance, Matthiessen [2] reported that the electrical conductivity of a copper wire, measured at 0°, changed if it had been heated to 100° and then cooled. This is not a case of true allotropism but is merely the result of a lag in the attainment of equilibrium. It can be overcome by repeating the oscillation of the temperature a sufficient number of times. The equilibrium then becomes established, and the resistance of the metal assumes a perfectly definite value.[1]

---

[1] Hulett, Z. physik Chem., *37*, 385 (1901). See, however, the criticism of this study by Balareff, Z. anorg. allgem. chem., *145*, 122 (1925) and by Schoorl, Z. physik. Chem., *160*, 158 (1932). Glasstone, J. Chem. Soc., *119*, 1689 (1921) applied Hulett's interpretation to a study of red and yellow lead monoxide.

[2] Matthiessen and von Bose, Pogg. Ann., *115*, 353–397 (1862).

If there is still doubt whether the two samples are identical, the following methods may be employed:

(a) The addition of a different substance to a given sample usually lowers its melting point. If the two samples are of the same material, the melting point will remain unchanged after mixing them. Two acids have the formula $C_{24}H_{28}O_2$, namely lignoceric acid (m.p. 80°) and tetracosanic acid (m.p. 86°). To prove the difference in their constitutions, Meyer [2] determined the freezing-point curve of their mixtures. It passes through a minimum at 79°.

It should be noted, however, that this criterion may fail in unusual cases. For instance, 2,6-dichloro- 4-bromo- and 4,6-dibromo- 2-chloro- oxybenzaldehyde have exactly the same melting point (105°) and they form a continuous series of mixed crystals, all melting at this same temperature.[3]

(b) If it is difficult to determine the identity of the crystalline forms of two samples, tests may be made to discover whether a crystal of one of them will serve as a nucleus for the crystallization of the other. The conditions of the test must be such that other powders will have no effect. In experiments of this type, however, it is necessary to beware of *isomorphic nuclei*, whose presence might lead to erroneous conclusions.

(c) Cohen, in 1894, demonstrated the value of measurements of electromotive forces in solving this problem. If a cell is constructed with each of the electrodes consisting of one of the materials to be compared and immersed in the same solution, an electromotive force will be detected only if these specimens are really different. In this way he [1] determined the temperature (20°) at which white tin goes over into grey tin. Placed side by side in a solution of pink salt (tin ammonium chloride) they develop an increasing electromotive force, positive or negative, when the temperature is raised above, or lowered below, 20°. At this temperature, equilibrium is established and no electromotive force is generated. This is the transformation temperature; the two varieties of tin are clearly different.

---

[1] Cohen and Holdermann, Z. physik. Chem., *87*, 419 (1914); Burgess and Kellberg, J. Wash. Acad. Sci., *5*, 657 (1915).

[2] Meyer, Bred and Soyka, Monatsh., *34*, 1113 (1913).

[3] Lack and Nottes, Ber., *68*, 1200 (1935).

B. *Polymorphism and Isomerism*

After two specimens of identical composition prove to have different properties it must still be determined whether their relationship is that of isomers or polymorphs. If they are isomers, the two species of molecules constituting them are not alike and the difference persists in the liquid state. If they are polymorphic forms the difference resides only in the crystalline network and disappears with it.

Applications:

(a) Isomers alone differ in the liquid state. For instance, octahedral and prismatic sulfur form an identical liquid on melting. They are, then, polymorphic forms of the same material. Sulfur μ which Smith [2] differentiated from sulfur λ by its solubility in carbon bisulfide, is an isomer of the latter, because they exist together in melted sulfur, in proportions varying with the temperature.

---

[1] Cohen and van Eyk, Z. physik. Chem., *30*, 601 (1899).

[2] Smith, Holmes and Hall, Z. physik. Chem., *52*, 602 (1905).

(b) Two isomers or two polymorphs always have different solubilities in the same solvent, but only isomers produce solutions whose properties are different at the same concentration and at the same temperature. For instance, red and yellow mercuric iodide are polymorphs because their solutions in potassium iodide have the same density at the same temperatures and concentrations. On the contrary, green and violet chromic chloride hexahydrate are isomers because when their solutions are treated with silver nitrate, all the chlorine is precipitated from one, but only one third from the other.[1]

The method of Singh [2] is a nice application of the same principle to the study of optically active compounds. The rotatory power in solution is identical in the case of polymorphic forms, but is not the same for tautomers or isomers. However, the curves of the rotatory dispersion of two different substances may meet at a point corresponding to a certain wave length, and so indicate an identical rotatory power of the two, but at this wave length only. It follows that two isomers may appear, under such circumstances, as polymorphs. In order to avoid this error it is necessary to measure the rotatory dispersion. For polymorphs, the values will be identical over the whole range of the spectrum under consideration; for isomers the values will be different. Thus it was shown that the three forms of ortho-iodophenylimino camphor are polymorphic forms and not isomers.

(c) If two isomeric compounds are placed in intimate contact, either in the liquid state or in the presence of a solvent, they exist together and form mixtures, while the less stable of two polymorphic forms will disappear completely. For instance, if ordinary tin is placed in contact with grey tin below 15° it is finally transformed wholly into the latter (tin pest). In contrast, Chavanne[1] found that the two stereochemical isomers of acetylene dichloride $(CHCl)_2$ form an equilibrium mixture:

---

[1] Werner and Gubser, Ber., *34*, 1579 (1901).

[2] Singh, J. Indian Chem. Soc., *6*, 1007 (1929).

	Density $\frac{15°}{4°}$
cis form	1.2913
trans form	1.2651
equilibrium mixture (20% transformed)	1.2863

(d) The more stable of two polymorphic forms always has the higher melting point and the lower solubility, while no such prediction is possible for isomers. (For definition of "isomer" see note, p. 35.)

	Melting Point			
Polymorphs:	Stable		Metastable	
Sulfur	Monoclinic	+120°	Triclinic	+114.5°
Isomers:				
Benzaldoximes	Anti:	+35°	Syn:	+130°
Aldehyde	Paraldehyde	+12.5°	Acetaldehyde	−123.3°

(e) A very ingenious application of the same principles was made by Sidgwick[2] in his cryoscopic method of differentiating between isomers and polymorphs. A saturated solution of the more soluble form (*A*) is prepared and some crystals of the second form (*B*) added. If *A* and *B* are polymorphs, *B*, the less soluble, is the more stable. *A* changes into *B*, which serves as a center of crystallization, and the concentration of the saturated solution falls. If, on the contrary, *B* is an isomer of *A*, it will dissolve in the common solvent without affecting the solubility of *A*, and the concentration of the saturated solution will increase. The changes in the concentration of the saturated solutions are followed by determining cryoscopically the temperature at which they begin to freeze. For example, para-nitrophenol exists in two forms, one (*A*) pale yellow, stable toward light, the other (*B*) reddens when illuminated. A saturated solution of pure *A* in benzene shows a cryoscopic depression of 0.224°; the corresponding figure for a saturated solution of pure *B* is 0.249°. Therefore, *B* is more soluble than *A*. If crystals of *A* are added to the saturated solution of *B*, the solubility decreases, because, after a short time, the depression is only 0.243°. Consequently, these two materials are polymorphic forms of the same compound.

---

[1] Chavanne, Bull. soc., chim. Belg., *26*, 287 (1912).

[2] Sidgwick, J. Chem. Soc., *107*, 672 (1915).

Benzoylcamphor has an enolic and a ketonic form: $C_{10}H_{15}O \cdot CO \cdot C_6H_5$ and $C_{10}H_{14}O \cdot C \cdot OH \cdot C_6H_5$. The enolic form is the more soluble in benzene and gives a cryoscopic depression of 4.9°. On adding the less soluble ketonic form, the depression soon reaches 7°. Therefore, they are isomers.

CHAPTER VI

STATIC AND DYNAMIC ISOMERS

If the kinetic theory is accepted, a solution is a phase whose molecules are not all identical, as in a pure material, but they belong to two or more different types. There is, then, no warrant for believing that the mutual actions of these different molecules are the same in the pure liquid as in the solution, and so the latter acquires particular properties. Each solution then constitutes a new species, whose properties are not necessarily the mean of those of its constituents. Experience has often confirmed this statement and it is now necessary to treat solutions as chemical species of a particular type.

A pure material consists of identical molecules, while a solution contains different kinds of molecules. How then should polymerized materials be classed? True, they contain several species of molecules that are polymers of each other, but these are inseparable. For example, water is made up of H_2O, $(H_2O)_2$, $(H_2O)_3$. The equilibrium persists because of the high velocity of the reciprocal transformations of these molecular species. The study of pseudo-systems will show how this difficulty may be surmounted.

Suppose that the various types of molecules forming a solution have the same percentage composition and differ only in molecular weight, structure, etc. This solution is known as a *pseudo-system* because, depending on conditions, it will behave as either a solution or a pure compound. For instance, acetylene, C_2H_2, and benzene, C_6H_6, both stable in the cold, transform into each other at high temperatures in the presence of porcelain. Consequently at low temperatures their mixture is a solution, but at high temperatures it behaves as a single substance.

It is often possible, with the aid of suitable catalysts, to bring about at will, either the conservation of forms in apparent equilibrium or, on the contrary, their quasi-instantaneous transformation. In such instances, a pair of *dynamic isomers* is involved. From the molecular standpoint these always constitute a solution, but studied with the aid of the criteria of the phase rule, they behave sometimes as solutions and sometimes as pure compounds.

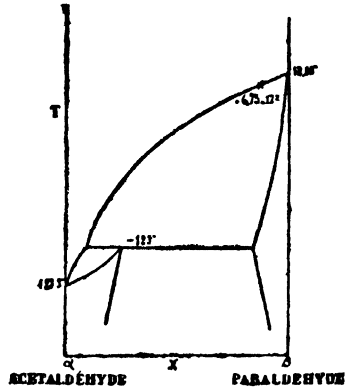


FIG. 9. Freezing-point curve of the system: acetaldehyde plus paraldehyde.

An excellent example of this is the system: acetaldehyde + paraldehyde [$C_2H_4O + (C_2H_4O)_3$], studied by Hollmann.[1] In the cold and in the absence of a catalyst, these two compounds are stable and may be mixed in all proportions. The system acts then as a solution; acetaldehyde melts at −123.3°, paraldehyde at +12.55° and their mixtures at intermediate temperatures (Fig. 9). However, the addition of traces of sulfuric acid to the mixture catalyzes the mutual transformation, and a stable equilibrium between the two polymers is established at each temperature. The composition of the system in equilibrium varies with the temperature, the liquid phase becoming richer in acetaldehyde as the temperature rises. On freezing, only paraldehyde crystallizes out, but the catalyst acts in proportion as the concentration of acetaldehyde in the liquid tends to rise; the equilibrium is immediately reestablished, and the composition of the liquid remains unchanged throughout the freezing. For the same reason, the temperature remains constant during the separation of the solid, as in the case of a pure substance. In this way, the *natural* freezing point (6.75°) of the system corresponding to a solution of invariant composition (11.7 mole % acetaldehyde) is determined, and in the same manner there can be obtained other *natural* constants of this mixture, such as the boiling point (41.6°), density, viscosity, etc.

---

[1] Hollmann, Z. physik. Chem., *43*, 129 (1903). See also the later experiments and the more complete theory of Smits and de Leeuw, *ibid.*, *77*, 269 (1911) and Smits' book, *The Theory of Allotropy,* translated by Thomas. London (1922).

Many similar cases have been discovered since chemists turned their attention to this problem. The diverse varieties of melted sulfur, and the mixtures of oximes formed from pairs of stereoisomers, have been particularly well studied from this standpoint.

To summarize, the difference between isomers and associated compounds is entirely relative. This is shown plainly by the classification of the types of isomers, proposed by Lowry and Steele:[1]

(a) *Static* isomers[2] are stable and each is a definite compound; their mixture is a solution. Examples, $C_2H_2 + C_6H_6$; propionaldehyde + acetone.

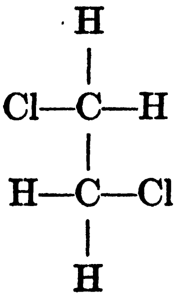
---

[1] Lowry & Steele, J. Chem. Soc., *107*, 1382 (1915).

[2] The term isomers is used here, as by its coiner Berzelius, to designate

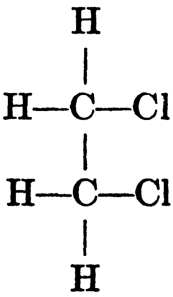
(b) *Dynamic* isomers behave differently depending on conditions:
(1) In the absence of a catalyst or in the presence of a negative catalyst (SO_2 for melted sulfur, for instance) they behave like static isomers and form pseudo-binary mixtures;
(2) In the presence of a positive catalyst (NH_3 for sulfur) they behave like definite compounds and form unary systems (acetoacetic ester).

(c) *Tautomers* are desmotropic substances, for which two or more molecular structures are admissible, but the different constituents can never be separated. Under all circumstances they behave as spontaneously transformable dynamic isomers. Such are: polymerized compounds (water); "motoisomers" in which the position of the double bonds of the benzene nucleus oscillates continually (1,2- and 1,6-dichlorobenzene); stereoisomers with single bonds, all of whose forms are equivalent in the liquid state because of the freedom of rotation of the different radicals around the single bond which unites them. An example of the latter case is:



$$\begin{array}{c} H \\ | \\ Cl-C-H \\ | \\ H-C-Cl \\ | \\ H \end{array}$$

and



$$\begin{array}{c} H \\ | \\ H-C-Cl \\ | \\ H-C-Cl \\ | \\ H \end{array}$$

materials of the same empirical formula. This is contrary to the usage introduced later into organic chemistry limiting the use of this term to denote metamers in opposition to polymers, and requiring that to be considered isomers two substances must also have the same molecular weight.

Polymorphic forms themselves may be considered as representing the crystallized state of stereoisomers corresponding to different tautomeric forms in equilibrium in the liquid. If this viewpoint is accepted, the distinction between polymers and isomers becomes more and more slight. In cases such as those of the chalcones studied by Weygand [1] it would seem more prudent, under the existing conditions, not to distinguish between these two classes, but to include them both in the term "crystalline forms."

The idea of dynamic isomerism found a new and very important field of application as a result of the extremely interesting studies of Baker and of Smits [2] on the extraordinary changes in properties observed in materials subjected to intensive desiccation by the prolonged action of phosphorus pentoxide *in vacuo.*

In 1922, Baker [3] showed that pure benzene, after such treatment, boils, under normal pressure, not at 80° but at 109°. At the same time, judging from the temperature coefficient of the surface tension (method of Ramsey and Shields), the degree of association of the liquid was considerably above unity. This result was entirely unexpected, since this compound, up to that time, was considered as typically normal and not polymerized.

The interpretation of these facts was given immediately by the theory of allotropism, which Smits had developed several years previously. According to him, the majority of pure materials do not consist of identical molecules, but of an intimate mixture of different species of molecules

---

[1] Weygand and Baumgärtel, Ann., *469*, 225 (1929); Weygand, Mensdorf and Strobelt, Ber., *68*, 1825 (1935).

[2] A general discussion of this topic is given by Smits, Rev. gen. sci., *37*, 265 (1927); J. Chem. Soc., *129*, 2655 (1926). See also Smith, *The effects of moisture on chemical and physical changes.* London (1929).

[3] Baker, J. Chem. Soc., *121*, 568 (1922).

(metamers or polymers), in statistic equilibrium with each other and inseparable under ordinary experimental conditions. They are, then, typical *tautomers.*

He believes that, as a result of intensive desiccation, the reversibility of the polymerization reaction:

$$n(C_6H_6) \rightleftharpoons (C_6H_6)_n$$

will cease, at least partially; the original equilibrium will thus be progressively disturbed so as to raise the proportion of the polymerized molecules.

If this conception is valid, the result of prolonged desiccation would be that the benzene should behave as a mixture of more or less stable isomers, which could be separated, at least to some extent, by a suitable method of fractionation. In fact, Baker, in 1924, showed that during distillation, the boiling point of this extremely dry benzene rose from 80° to 87°, and at the same time the pressure of the saturated vapor fell.

These studies open up great possibilities, and already have materially aided in the elucidation of several problems hitherto unsolvable. Cases in point are the equilibria between the polymorphic forms of phosphorus, and the paradox presented by ammonium chloride which, moist or dry, seemingly has the same vapor pressure, although the density of the vapor varies up to twice its value.

In this field, there apparently has been reached one of those particularly significant stages of scientific progress when certain points of view hitherto considered impregnable will have to give way before the onslaught of new facts. An original rigid classification must have its bounds enlarged to adapt it to new observations, without abandoning, however, the fundamentals of the advances which the researches of the last century have brought.

CHAPTER VII

SYSTEMS NOT IN STABLE THERMODYNAMIC EQUILIBRIUM

THE criteria of the phase rule, used in the preceding chapters to make the definitions precise, deal essentially with polyphasic thermodynamic equilibria. Usually stable equilibria are involved though, in certain cases, as has been shown, metastable equilibria, such as those of dynamic isomers, need to be considered. There also have been pointed out the complications arising in the consideration of systems where the criteria of definition are not purely thermodynamic as, for instance, the mixtures of optical antipodes. The present chapter will discuss the extension of the preceding definitions to include: (A) the case in which the thermodynamic equilibrium is not of the greatest possible stability, (B) where the equilibrium is not purely thermodynamic, (C) where the system under consideration, far removed from being in equilibrium, is in a state of transformation.

(A). There are systems in metastable thermodynamic equilibrium, where the equilibrium attained is not the most stable of all the possible equilibria. For instance, supercooled water is in metastable equilibrium with its saturated vapor because a more stable state of equilibrium is reached when the liquid freezes. Likewise, all the constants of the heterogeneous equilibrium of nitroglycerine can be carefully measured, but a much more stable equilibrium is established spontaneously when this material explodes.

The relative stability of an equilibrium, then, can be judged only by comparing it with other states of equilibrium that actually exist under like conditions. It follows that one can never be sure of attaining the most stable equilibrium. For example, glycerine, supercooled at 0°, was thought to be in stable equilibrium until a fortuitous circumstance caused its crystallization at that temperature. In the same way, the double ammonium salt of sulfuric and nitric acid was considered stable until the explosion at Oppau (1921) showed that this was merely a case of metastability.

The part played by *seeds* (centers of crystallization) and by *detonators* is quite important in evaluating the stability of an equilibrium. From this point of view, there must be kept in mind the rule of successive transformation stated by Ostwald:[1] the passage from an instable to a stable state is not usually direct, but there are halts, more or less prolonged, at each of the intermediate metastable states. It should cause no surprise if a material retains its liquid state when it is salted out of its solution, even though there was every reason to believe that it would separate in the crystalline form at the temperature of the experiment. There is formed first a liquid, rich in the material expelled from the solution, but it also contains a little solvent and dissolved salt, so that there is produced a metastable equilibrium between the two saturated liquid phases. It is well known that it is difficult to make materials crystallize under such conditions, because the other components act like some sort of impurity and delay the appearance of centers of crystallization.

---

[1] Ostwald, Z. physik. Chem., *22*, 306 (1897).

False equilibria, like those discussed by Duhem,[1] are often difficult to distinguish from metastable equilibria. If detonating gas liquefies at a low temperature like a mixture of any other gases, the metastable equilibrium of liquefaction thus obtained is nevertheless, from the chemical point of view, a state of false equilibrium. In fact the equilibrium of reaction differs according to whether liquid water or the gases resulting from its dissociation is the starting point.

In the study of systems in false equilibrium, the role of catalysts is enormous, particularly in organic chemistry, which van't Hoff declared to be "the world of materials in false equilibrium." Consequently, all such compounds tend spontaneously to react so as to reach states of greater stability. However, the final state of the system will vary in proportion as traces of specific catalysts favor this or that type of decomposition at the expense of all the other possible modes. The studies by Sabatier of the decomposition reactions of organic vapors in the presence of different catalysts provide numerous examples in which such phenomena have been followed quantitatively.

To sum up, the state of all these systems in metastable or in false equilibrium is adequately defined only if there is detailed knowledge of the conditions of the medium and also of the presence of nuclei or of catalysts capable of acting on the system.

(B) In addition to these systems in which stable thermodynamic equilibrium exists there are others where this equilibrium is not of a purely thermodynamic character.

Under ideal conditions, where thermodynamics can be applied, no account is taken of the disturbing influences of molecular forces, of gravity, of electrical energy, etc. However, in practice it is impossible to attain these limited conditions in an ideal manner, and frequently the perfectly stable equilibrium of a system can be explained only by taking account of the active intervention of forces whose effects are ordinarily considered negligible. A case in point is furnished by colloids, very stable systems whose equilibrium, paradoxical from the viewpoint of pure thermodynamics, can be accounted for by the van der Waals' forces, the Brownian movement, the existence of electrical charges, etc. Similarly, certain equilibria are photochemical (anthracene and dianthracene).[1] Such systems are completely characterized only if the value of these new determining factors is stated.

---

[1] Duhem, *Thermodynamics and Chemistry*: Translated by Burgess: New York (1903).

The molecular theories also are frequently inadequate in such cases. There is, for example, no method of determining *accurately* the molecular weight of molecules as large as those of hydrated silica, etc. Therefore, it is useless to try to decide definitely whether solutions of such materials contain free molecules or polymolecular particles. This question has no longer a precise meaning, and with it, in this extreme case, disappears any attempt at differentiation between true and false solutions.

The differentiation between solutions and aggregates also presents real difficulties at times. Instances are provided by the attempts to decide whether a system whose particles have an extremely high degree of dispersion is monophasic or polyphasic, or cases where the constituent molecules are relatively large.[2]

The different phases of an aggregate can usually be separated without difficulty by mechanical means (heavy liquids, magnetic attraction, etc.), or they can be distinguished, more or less easily, with a microscope. Sometimes it is necessary to use an ultra-microscope to detect an heterogeneity (smokes, stable suspensoids, critical opalescence, etc.) but unfortunately this latter method is too sensitive, because it may falsely indicate a lack of homogeneity in solutions that really are quite normal. Thus, Spring [1] showed that optically empty solutions of salts of the alkali metals may be prepared, but this is impossible, probably because of hydrolysis, with salts of heavy metals. These, however, have always rightly been considered to form true solutions.

---

[1] Luther and Weigert, Z. physik. Chem., *51*, 297 (1905).

[2] Lumière, Rev. gen. colloides, *3*, 161 (1925).

Likewise, colloidal solutions produced by dispersing a solid in a liquid (colloidal metals) are aggregates. But how are solutions of albumin to be classified? Are the molecules of this material so large that they function as small particles, or are these systems, as was shown by Sörensen,[2] true solutions obeying the phase rule, and exhibiting simply to an extreme degree peculiarities ordinarily much less developed (e.g. imperceptible freezing-point depression)?

Actually, these difficulties are surmounted easily if the relativity of the definitions given at the beginning of this book are kept in mind. They should be applied only in their proper sphere. The very act of using the phase rule entails a disregard of all physical factors other than temperature and pressure. In a colloidal system where these factors are no longer negligible, the phase rule cannot be applied with certainty.

(C) There still remains the inquiry regarding the characteristics necessary to distinguish unequivocally physical transformation (e.g. progressive crystallization) from chemical transformation (e.g. reaction). This evidently requires, first of all, a clear knowledge of the reactants present at the beginning and at the end of the reaction. Next it is equally necessary to determine the path and the intermediate compounds whose formation reveals the mechanism of the reaction. Finally, the equilibrium constant and the speed of the transformations ought to be known, as well as the elapsed time since the start of the reaction.

---

[1] Spring, Bull. acad. roy. Belg. Classe sci., p. 300 (1899); Oeuvres complètes, vol. I, p. 833 (1914).

[2] Sörensen, J. Am. Chem. Soc., *47*, 457 (1925).

With all these values at hand it should be possible to define, at each instant, the state of the system being examined. These data play an important part in organic chemistry and in the study of radioactive transformations. However, they are of no interest, even if they could be determined, for ionic reactions, which are practically instantaneous.

CHAPTER VIII

OBJECTIONS TO PARTICLE OR CORPUSCULAR THEORIES

In the preceding chapters it has been shown how the facts have required the chemist to distinguish the various types of materials, and how, by means of the phase rule, their characteristic differences can be defined precisely. These ideas have found an interpretation in the molecular and atomic theory and are expressed by structural formulae. This symbolic language has become indispensable to the chemist because of the number and the complexity of the substances he studies. Is there complete accord between these formulae and the facts? Does each formula correspond to a single chemical species, and is each species represented by a single formula?

According to the particle theory the smallest chemical units of matter (electrons and ions excepted) capable of independent existence are *molecules,* themselves composed of one or more identical or different atoms. This premise leads to definitions that at first sight seem very clear:

Elements consist of *identical molecules* containing a *single species* of *atoms:* O_2, S_8, P_4, Hg, etc.

Compounds consist of *identical molecules* each containing *several species* of *atoms:* NaCl, CH_4O, etc.

Solutions are made up of *two or more species of molecules* intimately *mixed:* solution of sugar in water, isomorphic crystals, etc.

The application of these terse definitions encounters certain obstacles. Those dealing with elements will be examined first.

The atomic theory, as Dalton conceived it, regards a simple substance as formed by the juxtaposition of atoms, all with identical properties and having equal and invariable mass. This idea, regarded as obvious, for a long time withstood the test of experimental examination. The studies of Stas [1] confirmed, with great precision, one of the postulates arising from it: "The constancy of composition of every compound does not prove that the proportions by weight exhibited by their elements are maintained *absolutely* in the compounds with other materials. For instance, the composition of barium sulfate and of barium sulfide may each be constant and yet the ratio by weight of sulfur to barium in the sulfide need not be absolutely identical with the ratio between the same elements in barium sulfate." Stas' determinations showed that the identity of such relationships persisted in all the cases investigated. This justified, *a posteriori*, Dalton's ideas.

However, from another point of view, Dalton's hypothesis proved inexact. The atoms of a single chemical element do not always have the same mass and their mass is not invariable. Two atoms of the same mass do not always belong to the same element. These are the conclusions that have come from the researches of the last twenty-five years on the phenomena of radioactive disintegration.

---

[1] Stas, Nouvelles Recherches sur les Lois des Proportions Chimiques (1865), Oeuvres complètes, vol. 1, p. 424, Brussels (1894). See Scott, J. Chem. Soc., *111*, 303 (1917) who has discussed "The Atomic Theory with special reference to the work of Stas and Prout's hypothesis."

According to Rutherford's [1] hypothesis, every atom consists of a nucleus, which makes up its principal mass, surrounded at relatively great distance by N planetary electrons. The nucleus itself consists of K electrons and K + N charges of positive electricity ("the proton," whose mass equals that of the hydrogen atom). N is the atomic number, that is, the ordinal number of the element in the periodic system. Moreover, since Moseley's [2] work, it is known that an element is characterized essentially not by its atomic weight but by its atomic number. It follows then that two atoms having the same number N of peripheral electrons may possess $K_1 + N$ and $K_2 + N$ protons, sums that are slightly different if the number of electrons in the two nuclei are K_1 and K_2. The masses of these atoms will then be different as well as all the properties derived from the mass (atomic weight, density, rate of diffusion, electrochemical equivalent, etc.), but all their other characteristics (charge, spectrum, valence, chemical properties) will be identical. Conversely, two atoms having the same mass but different numbers of peripheral electrons belong to different elements. The first type are known as *isotopes*, the others are *isobars*.

Examples: Soddy and Fajans [3] showed that several series of radioactive atomic disintegration resulted in lead, an end product. According to their origin, the atoms of these diverse lead isotopes have a weight of 206 (from uranium) or 208 (from thorium). Ordinary lead (atomic weight 207.2) is then a mixture of these two isotopes. These views have been confirmed, notably by:

(1) exact atomic weight determinations using lead salts

---

[1] Rutherford, Phil. Mag., [6], *22*, 669 (1911).

[2] Moseley, Phil. Mag., [6] *26*, 1024 (1913).

[3] Soddy, Chem. News, *102*, 422 (1913) and *103*, 168 (1913); Fajans, Physik: Zeit., *14*, 131 (1913).

of different origins. The values obtained ranged from 207.90 ± 0.013 to 206.04 [1]

(2) measurements of the solubility in water, at 25°, of two lead nitrates of different origins. The solubility was found to be 1.7992 ± 0.013 gm. molecules per liter, which in grams amounts to 37.281%, for ordinary lead, while the nitrate prepared from lead coming from a source rich in uranium gave a corresponding value of 37.130%.[2]

(3) determinations of their melting points, examination of their spectra, etc. These are practically identical for the different samples.

The case of hydrogen is still more complicated because allotropism and isotopy are encountered here, side by side. In the first place, the discovery of heavy water has provided a convenient raw material for the preparation of deuterium, whose atomic number is 1, like that of ordinary hydrogen, but whose nucleus has twice the mass of the hydrogen nucleus. In contrast to the observations on other pairs of isotopes, the physical constants of hydrogen and of deuterium are quite different:

	Boiling Point	*Triple Point*
H = 1	−252.78°	−259.24°
D = 2	−249.66	−251.58

On the other hand, the diatomic molecule of ordinary hydrogen presents a singular case of allotropism. Unlike ozone and oxygen, ortho- and para-hydrogen differ, not in the number of atoms in the molecule but in the direction of the rotation of the two atomic nuclei of the molecule. If the rotations are in the same direction the sample is ortho-hydrogen, if they are opposed it is para-hydrogen. Ordinary hydrogen is a mixture, in equilibrium, of these two allotropic forms (at 84° abs. it contains 50% of each). The difference in constitution is reflected in the physical constants:

---

[1] Fajans, Z. Elektrochem., *24*, 163 (1918); Hönigschmidt and Horovitz, Monatsh., *36*, 354 (1915).

[2] Richards and Schumb, J. Am. Chem. Soc., *40*, 1403 (1918).

	Boiling Point	*Triple Point*
H_2 ordinary	20.39° abs.	53.9 mm. Hg
H_2 para	20.26	53.0

Aston's[1] researches have demonstrated the possibility of recognizing also the existence of isotopes of elements which are not of radioactive origin. He uses the method of positive ray analysis invented by Thomson.[2]

These rays are formed by the rectilinear projection of ions (atoms or radicals bearing one or more charges of positive electricity). Under the action of an electromagnet, these rays are deviated through an angle proportional to the ratio of the mass to charge, $\frac{m}{c}\cdot$ For identical charges, a non-homogeneous beam of positive rays will then produce a mass spectrum, recorded photographically, of which each ray corresponds to a given atomic mass. This may be measured to about 1/10,000th, by comparison with rays of known mass.

This method has shown that the following elements are homogeneous:[3] He, Be, F, Na, Al, P, Sc, V, Mn, As, Y,

---

[1] Aston, Nature, *104*, 334 (1919) ff.; and his *Mass Spectra and Isotopes*, revised ed. London (1933).

[2] Thomson, *Rays of Positive Electricity and Their Application to Chemical Analysis*, 2nd. ed. London (1921).

[3] International Table of Stable Isotopes for 1938.

Cb, I, Cs, La, Pr, Tb, Ho, Tm, Lu, Ta, Au, Bi, Th. All of these elements have uneven atomic numbers, except the first two, He and Be, and the last one, Th. The other elements contain 2, 3, 4 or more isotopes in varying proportions. Tin has the greatest number 10; the atomic masses of these tin isotopes range from 112 to 124.

Radioactivity has produced several examples of isobars in addition to these numerous isotopic elements. The atomic weights are the same, but the chemical properties and atomic numbers are different. For instance, the principal isotope of calcium and the principal isotope of argon both have the atomic mass 40, nevertheless these isobars are quite different chemically.

To sum up, an element can no longer be characterized by its atomic weight (that sometimes is quite variable) but by its atomic number. The latter determines its chemical properties, even though some of the physical constants differ. That which remains invariable in a simple substance is not the whole atom, as Dalton believed, but only the number of free positive charges of its nucleus. This is the definition adopted by the International Committee on Chemical Elements.[1]

With respect to the phase rule, an element composed of several isotopes will not always behave as a hylotropic phase, and will then no longer be a simple substance. To the analyst, however, it will remain no less a homogeneous material, always exhibiting the same reactions.

The application of the atomic and molecular theory to definite compounds and solutions leads likewise to a more extended analysis of the inner constitution of such chemical systems than is possible by the purely thermodynamic method of the phase rule. The conclusions reached are less certain but more detailed.

---

[1] Urbain, Bull. soc. chim. Belg., *36*, 124 (1927); see also the discussion at the First Conseil de Chimie Solvay, p. 21. Paris, (1922).

Thus, structural formulae permit the representation of the constitution of many forms of tautomers or complexes, whose existence cannot be indicated by the methods of the phase rule. This information, such as the formation of colored solvates, dissociation of ionizable complexes, the presence of free radicals or of activated molecules participating in chain reactions, comes from the interpretation of quite varied tests such as absorption spectra, electrical conductivity, etc.

The characteristics indispensable to the complete knowledge of a given chemical system can be summed up as follows:

An element is fundamentally characterized by the structure of its atoms. Before the discovery of isotopes, the mere knowledge of the atomic weight sufficed to establish what element was in question, but now it is necessary to know also the mass and the concentration of each isotope present in the sample. For instance, many of the well-determined characteristics of a sample of "pure" lead depend on the proportion of the metal originating either from thorium or from uranium.

A chemical individual, i.e. a compound or element, is symbolized by its molecular formula. It is necessary, then, to know:

(a) its qualitative and quantitative composition;

(b) its molecular weight, which makes it possible to differentiate between various polymers. If the association factor of a polymerized compound is known accurately enough the changes in concentration of the various polymers present can be followed quantitatively. However, the solution of this problem is still quite remote, even in the case of water;

(c) its chemical structure, as revealed by functional analysis, which gives the essential information for the differentiation of isomeric compounds;

(d) the stereochemical distribution of the atoms in the molecule.

When dealing with a solution, a knowledge of its concentration ordinarily suffices to remove all doubts as to its properties. However, since these properties are characteristics of the actions and reactions of mixtures of various molecular types, it is advantageous to know also to what category of solutions the system belongs. The possibilities are:

(a) ideal solutions whose constants may be deduced *a priori* from those of its components (chloro— + bromobenzene) with the aid of the theories of Nernst[1] and of Dolezalek;[2]

(b) solutions which have a region of partial solubility and whose properties obey much more complex laws as a consequence of the *physical* reactions of neighboring molecules on each other. The theory of mixtures of van der Waals[3] provides a detailed qualitative picture, that, however, is not quantitatively accurate (water + alcohols);

(c) solutions in which are formed molecular addition compounds, whose progressive dissociation greatly affects the properties (chloroform + ether);

(d) solutions of electrolytes which obey particular laws (water + HCl).

---

[1] Nernst, *Treatise on Physical Chemistry*, translated by Codd. London (1923).

[2] Dolezalek, Z. physik. Chem., *64*, 727 (1908):

[3] van der Waals, *Kontinuität* part 2, Leipsic 1900; and van der Waals and Kohnstamm, *Lehrbuch der Thermodynamik*, part 2, Leipsic 1912.

Purely chemical data as to the number and composition of the phases are insufficient to present an exact picture of aggregates. It is necessary to know, in addition, the respective masses of the phases, their degree of dispersion, and the entire *anatomy* of their constitution. However, that is beyond the limits of this discussion.

PART II

PURE MATERIALS

CHAPTER IX

HISTORY AND DEFINITION

PART I contained a detailed discussion of the steps necessary to define, without ambiguity, any chemical system. Next will be studied the methods by which a chemical system whose definition is given can be produced experimentally, and in close conformity to that definition. This question raises the problem of pure materials which, isolated or in mixtures, permit the preparation of all possible chemical systems.

A. *History of the concept of a pure substance*

All pure substances possess unchanging characteristics that distinguish them from one another. This idea goes back to antiquity.[1]

It was on this principle that Archimedes, in the 3rd century B.C., devised his method of determining densities in order to verify if the crown of Hiero, the tyrant of Syracuse, was pure gold or gold alloyed with silver. Here was an early application of the principle which is the basis of analytical chemistry: two substances with identical specific properties are said to be chemically identical.[2]

The systematic identification of substances by measuring their constants made some progress in the Middle

---

[1] Walden, *Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge*, pp. 62–73 Stuttgart (1910).

[2] Ostwald, *The Scientific Principles of Analytical Chemistry.* Translated by Gowan. London (1908).

Ages. The tables of densities drawn up by the Arabian scientists (e.g. Al Biruni, 1038) show this. In 1690, Robert Boyle recommended the use of density as an index of the purity of medicaments. Duhamel (1736) based his distinction of soda and potash on the difference of their solubility in water. In the 18th century more and more account was taken of the constancy of the properties of pure materials, and scientists, particularly the physicists, began to use these characteristics in standardizing measuring instruments. In 1724, Fahrenheit showed that the boiling point and freezing point of pure materials are characteristic constants, and Reaumur in 1730 recommended the use of alcohol as a thermometric liquid.[1] He described a method of purifying this compound, by which a product with the same properties could always be obtained.

Similar ideas were applied more and more in the 19th century by chemists in their study of the numerous substances encountered in their researches. Cavendish,[2] as early as the end of the 18th century, determined the constants of the gases with which he worked. Gay-Lussac,[3] in his classic studies on iodine and prussic acid, determined not only their boiling and freezing points, but also the vapor tension, density, crystalline form, solubility, and electrical conductivity. In 1832, in his papers on the benzoyl radical, Liebig [4] stressed the value of melting points as an aid in the identification of organic compounds. The importance of physical constants necessarily increased when isomerism was discovered.

Gradually the study of carefully purified materials was carried out in a more orderly manner. Stoichiometry, the science of the relations between physical constants and chemical structure, became autonomous. Berzelius, in his determinations of atomic weights, paid great attention to the preparation of pure materials. In 1842, Kopp [1] began a systematic study of the boiling points and the densities of organic compounds.

---

[1] Ostwald's *Klassiker der exakten Wissenschaften*, No. 57. Fahrenheit, p. 3; Reaumur, p. 23. Leipsic (1894).

[2] Cavendish, Phil. Trans., *74*, 119 (1784).

[3] Gay-Lussac, Ann. chim. phys., *77*, 128 (1811); *91*, 5 (1814).

[4] Liebig, Ann., *3*, 249 (1832).

The discovery of new physical properties provided additional criteria of purity and led to the isolation of numerous elements. Examples are: rubidium, caesium, gallium, thallium and germanium, characterized by their spectra; radium and all its congeners, isolated by reason of their radioactive properties.

In the last fifty years the idea of the absolute invariability of the constants of pure substances has been subjected to ever increasing precise verifications. Lockyer believed he had found that the luminous spectrum of metals varied with the temperature to which the vapor of the metal was raised. He thought that sodium, whose spectrum is always observed in the electric arc striking between electrodes of quite varied composition, arose from the partial dissociation of other metals. He made rather bold applications of these notions in astrophysics. Stas [2] wished to test if the experimental premises of this hypothesis were unassailable. At the conclusion of extremely careful studies, that extended over ten years, he succeeded in showing that the spectrum of a pure material is invariable, and the appearance of the characteristic lines of another element is due to the presence of traces of impurities, that can be eliminated if necessary.

---

[1] Kopp, Ann., *41*, 79 (1842) and ff.

[2] Stas, "Oeuvres posthumes," vol. 3 of his *Oeuvres complètes*, p. 202. Brussels (1894).

The English school has always been distinguished by its extreme care in purifying the organic materials whose physical-chemical properties were being studied. The researches of Perkin[1] on rotatory magnetic power are, in this respect, particularly remarkable. The long and detailed work of Young[2] on the experimental examination of the equation of state of pure liquids constitutes a model of this type of research.

B. *Definition of pure materials*

A material is pure if it is perfectly homogeneous after it has been subjected to successive modes of fractionating that are as different as possible. This definition requires some comment for its complete elucidation.

(a) It is indispensable to employ efficacious and varied methods of fractionation to verify the homogeneity of a pure material. Too often a single method of fractionation has been considered sufficient in making this test. If, by chance, the method adopted is not efficient (for instance if an azeotropic mixture is distilled) a simple mixture may be described as a definite chemical substance. It is obvious, that once the purification has been established with sufficient security, that only the most rapid and efficient method of obtaining the pure compound need be used.

A case in point is the following. A very sensitive indication of the presence of traces of gas dissolved in a liquid is given by verifying the constancy of the pressure of its saturated vapor, measured at constant temperature, from the beginning until the end of the vaporization of the liquid, or of the condensation of the vapor. The most volatile component will concentrate in the last bubbles of vapor that condense only under a notable over-pressure and vice versa.

---

[1] Perkin, J. Chem. Soc., *45*, 442 (1884); *61*, 287 (1892).

[2] Young, Sci. Proc. Roy. Dublin Soc., (N. S.) *12*, 374 (1910).

The carbon dioxide used by Andrews[1] contained about 1/1000th of air, consequently the liquefaction pressure rose 2.5% at the end of the operation. Young,[2] in contrast, succeeded in removing completely the dissolved gases from organic liquids used in his study on the equation of state. For instance, he measured the pressure of the saturated vapor of ethyl formate at 140°, while the relative volumes of the vapor and of the liquid varied within wide limits. His results were:

$\frac{V\ vapor}{V\ liquid}$	*Pressure in mm. Hg at 140°.*	
	I	II
0.5	7374	7358
1.0	7359	7367
1.5	7366	7366
2.0	7357	7371
Mean	7364	7366

These results are all the more remarkable since ethyl formate is quite difficult to preserve in the pure state because of its hygroscopicity.

(b) Crude samples of the same material but of different origins and methods of preparation usually have quite different physical constants. However, as the purification progresses these values converge toward a value which characterizes the pure material. In his classic studies of the properties of pure gases, Guye[3] particularly stressed the importance of starting with materials derived from different sources. This is the surest method of obviating the systematic errors arising from the unsuspected presence of impurities that are difficult to eliminate. There is every chance that these will differ with the origin of the respective samples, and will manifest their presence by the persistent discordance of the physical constants, and even after the purification if this is not particularly efficacious.

---

[1] Andrews, Chem. News, *21*, 101 (1870).

[2] Young, J. chim. phys., *4*, 434 (1906).

[3] Guye and Batuecas, J. chim. phys., *20*, 311 (1922) ff.

For instance, Baume[1] in his researches on methyl chloride used preparations from two different sources. The first was prepared by the action of hydrochloric acid on methyl alcohol, and its normal liter weight was 2.3045 gm.; the second, prepared from trimethylamine extracted from beet vinasse, after six fractionations, had a normal liter weight of 2.3065 gm., a decidedly higher value. By twelve additional fractionations this latter gas was separated into three fractions whose respective normal liter weights were: head, 2.3039 gm., middle, 2.3047 gm., tail, 2.3313 gm. This preparation evidently was contaminated by a material of high density. When purified, it showed (within the limits of experimental error, 1/10,000) the same normal liter weight as the first preparation. The two purified samples were identical, although the two preparations diverged noticeably in the crude state.

(c) The purity of a material is an entirely relative concept and differs according to the purpose in view.

For example, the purity of water to be used for checking the 100° mark of a thermometer is sufficient if the temperature of its vapor remains perfectly constant during the boiling. But such a sample is unsuitable for conductivity water, because it would contain traces of alkali derived from the glass vessels with which it had been in contact.

---

[1] Baume, J. chim. phys., *6*, 1 (1908):

In the same way, it is necessary to purify a substance with far more care when its index of refraction is to be determined to the fifth decimal place, than when the dielectric constant is to be measured, because it is difficult to determine the latter to within even 1/1000.

CHAPTER X

GENERAL METHODS OF PURIFICATION

This chapter deals with the preparation of pure materials derived from crude products or contaminated with impurities or secondary components that vary with the origin of the samples.

(1) In the preparation of pure materials it is well to start with commercial products of the best possible quality. In fact, the methods of purification by fractionating are particularly efficient when applied to large quantities of material, as is the practice in industrial establishments. Furthermore, these have available more varied facilities than the research laboratories: distillation with superheated steam, autoclaves, filter presses, etc. and they work under more economical conditions than the individual investigator.

But no matter how careful the manufacturer may be in purifying his products, the laboratory scientist must carry out a final fractionation of the materials he studies. Too many workers have (unfortunately) contented themselves with commercial products as delivered by manufacturers of established reputation, without taking the trouble to check the purity of these supplies. The chemical literature contains a superabundance of physical constants determined on materials of questionable purity, and hence these data are of no real value.

(2) It is often easier to eliminate harmful impurities

after subjecting them to a suitable chemical transformation.

For instance, wood spirit consists essentially of a mixture of methyl alcohol, methyl acetate and acetone. These are particularly difficult to separate from each other because their constants are so close together.

	Boiling Point	*Freezing Point*
Methyl alcohol	64.7°	−97.1°
Methyl acetate	57.5	−98.0
Acetone	56.1	−94.3

Therefore, the alcohol is converted into sulfonate or oxalate, or the acetone into its bisulfite compound. These products are solid at the ordinary temperature and consequently are easy to separate from the residual liquid.

Similarly, Mond's method[1] of separating cobalt and nickel is based on the ease with which the nickel combines with carbon monoxide. The formation of nickel carbonyl, a gas at ordinary temperatures, allows the complete removal of the nickel, while the cobalt, under these conditions, remains unchanged.

(3) When a product is prepared in the laboratory, it is better, during the course of the series of operations which are to lead to a pure material, to purify successively each of the intermediate products rather than to allow the impurities to accumulate in the final compound. The losses are higher, but an impurity that could not be removed later can often be eliminated at one of the earlier stages of the procedure. For example, when normal hexane is prepared from commercial propyl alcohol, it is essential to purify not only the alcohol but also the intermediate

---

[1] **Mond, Langer and Quincke, Chem. News, *62*, 97 (1890).**

product, the bromide. Commercial propyl alcohol contains appreciable quantities of isopropyl and isobutyl alcohol. It is almost impossible to eliminate these by fractional distillation, whereas the separation of the lower boiling bromides is relatively easy. The difference in the boiling points is greater, and the dephlegmators used are more efficient at the lower temperatures.

	Boiling Point	
	Alcohol	*Bromide*
Isopropyl	82.7°	59.5°
Propyl	97.4	71.0
Isobutyl	108.4	92.0

If the bromide is not purified, there will be formed, through the Würtz reaction, all of the following hydrocarbons, whose final separation is practically impossible:

	Boiling Point
Diisopropyl	58.1°
Methyl 2-*n*-pentane	60.0
n-Hexane	69
Dimethyl 2,4-*n*-pentane	83–84
Methyl 2-*n*-hexane	92
Diisobutyl	109.2

(4) The secondary reactions, which may result from the introduction of this new constituent into the original mixture, must be kept in mind when choosing purification reagents. It is necessary especially to beware of reagents capable of partially decomposing the material to be purified, and to avoid, if possible, the use of those that

might give rise to secondary products that are difficult to eliminate.

For example, commercial phosphorus pentoxide is not suitable for drying gaseous hydrogen chloride. It is often contaminated with trioxide, which can react with the gas to form volatile halogenated compounds of phosphorus that are very difficult to separate later from the hydrogen chloride. These troubles may be avoided by completely oxidizing the phosphorus oxide, by passing its vapors along with oxygen over heated platinum sponge, which catalyzes the oxidation.[1]

The following curious error of judgment illustrates the danger of not being sufficiently distrustful of traces of impurities contained in the starting materials or of those introduced by the reagents during the course of a preparation. Campbell[2] attempted to prove that the two antipodes of camphoric acid do not have exactly the same physical constants, even when perfectly pure. He prepared the dextro acid by oxidizing camphor with nitric acid, while the laevo acid was obtained from *l*-borneol. A parallel purification of the two preparations resulted in samples that exhibited the following constants:

	Dextro	*Laevo*
Melting point	186.0°	186.5°
Solubility in gm./100 gm. of water at 40°	1.00	0.88
$(\alpha)_D^{18°}$	+51.8	−47.0

This proof would have been unassailable if he had also shown that these samples contained the same impurities at the beginning, since otherwise one of them might not have been really purified by the method chosen. To prove his case the worker should have treated both the products, *d* and *l*, in exactly the same manner, by starting with their common racemate. This could have been decomposed by a simple alteration of the temperature, as Pasteur did with the double tartrate of sodium and ammonium.

---

[1] Shenstone and Beck, J. Chem. Soc., *63*, 475 (1893).

[2] Campbell, J. Am. Chem. Soc., *53*, 1661 (1931).

The solubility of secondary butyl alcohol in water is exceedingly sensitive to the presence of alcohols or ketones. However, in the preparation of this alcohol by the reduction of methyl ethyl ketone the reaction is never complete, and the problem arises of eliminating traces of the ketone not exceeding several ten-thousandths. After vainly exhausting the usual reagents for ketones it might seem feasible to convert the alcohol into a non-volatile ester. There then arises the difficulty of recovering the alcohol by saponification. With aqueous potash the reaction is practically impossible; if alcoholic potash is used there is no certainty of removing the last traces of the ethyl alcohol introduced. The net result is merely the substitution of another difficulty for the original one. This can be circumvented by preparing the crystallizable mono-ester of a dibasic acid (phthalic) that is soluble in aqueous alkaline solutions, and consequently easily saponifiable without danger of introducing any harmful contaminant.

(5) It should never be forgotten that after a substance is obtained in a pure state it is generally very hard to keep it so.

Many materials are hygroscopic (e.g. acetic acid) or hydrolysable (e.g. esters). Others are oxidized by traces of dissolved air (e.g. aniline), or are sensitive to the light (e.g. phenol). The vessels in which these compounds are stored often yield traces of catalysts that hasten the production of decomposition products. For instance, Dutoit [1] found that alkali from the glass so accelerates the decomposition of acetone that it is no longer suitable in the study of the electrical conductivity of dissolved metal salts.

Finally, many materials are unstable when pure. In such cases it is expedient to add a small quantity of a stabilizer. For example, pure chloroform in contact with air decomposes spontaneously with formation of highly toxic phosgene. This reaction, slow in the cold, is so rapid at higher temperatures that it has always interfered with the measurement of the critical constants of chloroform. Therefore, and particularly when intended for medical use, chloroform is stabilized by the addition of several percent of alcohol. Likewise, polyphenols can be used to stabilize acrolein.[2]

---

[1] Dutoit and Levier, J. chim. phys., *3*, 435 (1905).

[2] Moureu, Dufraisse, Robin, and Pougnet, Compt. rend., *70*, 26 (1920).

CHAPTER XI

THEORY OF FRACTIONATION

(1) *Purpose.* A sample is fractionated in order to divide it into a series of portions, in which one property gradually changes because the impurities accumulate in the head or tail fractions. The efficiency of the process is a function of the separation.

The fractional distillation of a mixture containing equal weights of benzene and of toluene, as carried out by Young, is shown in the following table:

This table shows the quantities (in gm.) of liquid collected at the end of the condenser within the corresponding limits of the boiling point. In an efficient fractionation, the boiling temperature remains almost constant at the beginning and at the end of the distillation; the two components are distilling practically pure at these two stages. In the intervening range, the temperature rises rapidly, while the quantity of distillate is extremely small. In contrast, if the fractionation is quite ineffective, the boiling temperature rises regularly with the quantity of distillate; very little of the pure components will be collected; the distillate consists, for the most part, of mixtures, and little progress has been made toward separating them.

(2) *Fractional distillation* (theory). The theory of fractionation will be considered more intimately in the case of distillation, with the aid of *T-X* (temperature-concen-

FRACTIONATION OF 100 GRAMS OF A 50-50 BENZENE-TOLUENE MIXTURE
(ONE PASS; DISTILLATION RATE = 60 DROPS PER MINUTE)

Final Temperature	*Weights of Fractions*			
	Young Column Total height, 78 cm. Length of elements, 65 cm. 8 elements	Crismer Column Total height, 77 cm. Height of spirals, 65 cm. 55 spirals	Crismer Column modified by Miller Height of spirals, 73 cm. 95 spirals	
82.2°	12.2 gm.	20.5 gm.	80.2°	42.00 gm.
83.2	23.85	15.3	88.0	3.2
86.5	6.50	10.25		
92.3	5.05	2.50	106.0	1.3
95.4	1.40	0.80		
98.5	1.15	0.70		
102.0	1.05	1.20		
104.0	1.15	1.30	110.55	4.8
107.6	1.60	1.60		
110.0	3.95	2.05		
110.6	9.6	9.00	110.55	48.2
Pure toluene (by difference)	32.7	34.80		
	100.00	100.00		100.00
Remaining in column and condenser	6.25	3.50		6.50

tration) diagrams. The results obtained from these are directly applicable to fractional solidification, if the *V-L* (vapor-liquid) curves are replaced by *L-S* (liquid-solution).

Figure 10 presents the course of the *V-L* curves in the most simple case of isobaric distillation. The phases in equilibrium are given by the intersection of the horizontal corresponding to the temperature, under consideration, with the curves *V* and *L*. The liquid of X_l is then in equilibrium, at the temperature t', with the vapor, X_v. If it is possible to collect separately, from the condenser, this vapor X_v, the liquid thus formed, in its turn, will be in equilibrium with a new phase V, still more rich in component B, and so on. Starting with the liquid X_l, a process of this kind will finally produce a vapor composed entirely of pure B.

In practice, however, the facts are not so simple. When a distilling column is put into operation, the vapor X_v given off by the liquid X_l rises to a certain height, then condenses and flows back. During this reflux, this condensed liquid X_v comes in contact with new vapors X_v coming from the original liquid X_l. In the column, there will then be, returning liquid X_v in contact with a vapor of the same composition X_v. These two phases are no longer in equilibrium, and this will tend to establish itself in such a way that the returning liquid becomes richer in the less volatile component A; while the vapor, on the contrary, becomes richer in B. Everything that aids the intimate contact of the liquid with the vapor in the dephlegmator will therefore favor the separation of the components, because the vapor which reaches the top of the column is enriched in B and the residual liquid in the flask becomes richer in A. Finally, if the vapors rich in B

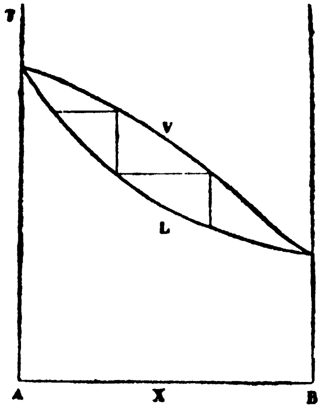


FIG. 10. Liquid-vapor equilibrium of a binary system at constant pressure.

are progressively removed from the mixture by condensation in the condenser, the hitherto unchanged equilibrium is progressively displaced toward the system rich in *A*.

The conclusion to be drawn from this discussion is that with a good dephlegmator it should be possible to collect separately quite different fractions at the first pass. The result thus obtained is equivalent to that possible only after numerous distillations in an apparatus not equipped with a fractionating column. The efficacy of this device is due to the intimate mixing of the returning liquid with the rising vapors.

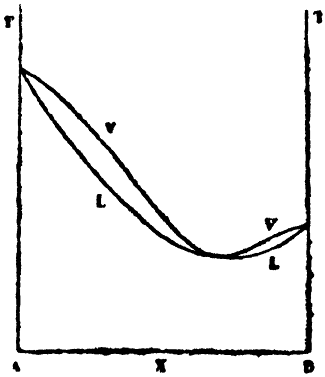


FIG. 11. Liquid-vapor equilibrium at constant temperature of a system forming a minimum-boiling azeotropic mixture.

(3) *Complications.* These arise from the complexity of the biphasic equilibrium diagrams, which do not always have the simple aspect assumed in Figure 10.

(a) The boiling point of a mixture X_m is a minimum (or maximum) (Fig. 11). This azeotropic mixture has remarkable properties. It behaves, to some extent, like a distinct component. Fractionation will result in the separation either of component *A* or of component *B* of the mixture X_m, but the latter will not be resolvable into its constituents.

For instance, aqueous alcohol forms an azeotropic mixture containing 95.6% alcohol and boiling at 78.15° at normal pressure. Consequently, anhydrous alcohol cannot be obtained by distilling any aqueous solution containing more than 4.4% water.

(b) The two components are not miscible at the boiling point, which is a minimum for the triphasic mixture (Fig. 12). The result of the distillation is the same as in (a). The vapor X has a composition between that of the two liquid phases, and functions again as a distinct component. The complete separation of the two components is therefore impossible in this case also. For example, the system water-aniline at 75°[1] shows the following composition (% aniline) of the three phases in equilibrium:

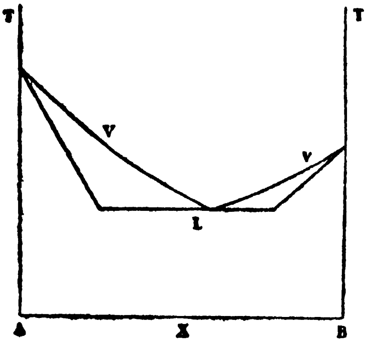


FIG. 12. Liquid-vapor equilibrium of a two liquid phase system at constant pressure.

$$\left.\begin{array}{l} L_1 = 3.2 \\ L_2 = 94.0 \end{array}\right\} V = 18.2.$$

If there are two liquid phases at the boiling point, but the latter is not a minimum, the composition of the vapor falls outside that of the liquid phases and the distillation proceeds normally as in (2). Isopentane + nitrobenzene is an example.

---

[1] Schreinemakers, Z. physik. Chem., 27, 95 (1898).

(c) The limiting case is encountered with two liquids that are practically insoluble in each other. They distil in the ratio of their partial vapor pressures. Only the component in excess can be obtained pure. Example: a mixture of water and essential oils.

This discussion leads to the general conclusion that a simple fractionation is not always capable of furnishing, in a pure state, all the components of a mixture. The operator must be sure that the components collected are not simply azeotropic mixtures. This assurance can be obtained by fractionating by two different methods (freezing and distillation, for instance), or by combining fractionation with an appropriate chemical treatment.

CHAPTER XII

FRACTIONAL DISTILLATION AND CONDENSATION

THE fractionation of liquefied gases takes place at a practically constant temperature, the pressure alone varies, and the vapors formed are passed through a portion of the liquid to increase the efficiency of the process. [See the description of the apparatus given by Baume [1] and Moles.] [2] In this instance also the passage of the vapor through the liquid increases the surfaces of contact and facilitates the establishment of the distillation equilibrium.

But in all other cases, the distillation is isobaric and is accomplished with the aid of dephlegmators. Consequently, these devices are of great importance to the laboratory and to industrial plants. In principle, they may consist of a simple vertical tube; the refluxing takes place on its walls, but the efficiency is minimal. The efficacy can be increased by lengthening the dephlegmator as much as possible; to avoid making it too high it can be formed into a zigzag or wound into a vertical spiral.

Very much better devices than these are available for use in the laboratory (Fig. 13). In the order of increasing efficiency they are: the Vigreux column,[3] easily constructed; Young's "evaporator still-head" [1] quite effective, but of rather delicate construction; the Darier column, filled with glass beads or metal spirals, that has the defect of holding back, by capillarity, a considerable quantity of liquid, which constitutes a net loss for the fractionation; the Dufton-Crismer column.[2] This is extremely efficient, easily constructed and not hard to clean. The vapor is forced to rise through a long spiral that is wet by the returning liquid, which forces the vapor to rise through all the coils. Its only defect is the ease with which it chokes with the condensed liquid if the dephlegmator is used at too high temperatures.

---

[1] Baume, J. chim. phys., *6*, 1 (1908).

[2] Moles, J. chim. phys., *14*, 408 (1916).

[3] Vigreux, Bull. soc. chim., [3] *31*, 1116 (1904).

Diagrams of the fractionating columns of

Young Crismer Vigreux

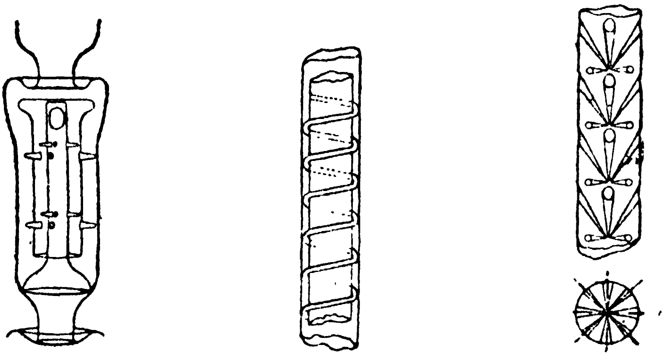


FIG. 13.

Miller [3] has remedied this fault of the Crismer column by placing the spirals farther and farther apart toward the base of the column. This facilitates the drainage of the returning liquid. He also fitted the column with an external heating coil, with an adjustable resistance, thus extending its serviceability up to about 200°. The table on page 71 shows the separatory power of several of these dephlegmators. This value, up to the present time an empirical quantity, has now been defined theoretically by Miller [1] as being measured by the free energy consumed in the more or less complete separation of two constituents, with a maximum coefficient of 100 when their separation is total.

---

[1] Young, J. Chem. Soc., *75*, 679 (1899); *Distillation Principles and Processes*, p. 13. London 1922.

[2] Crismer, Bull. soc. chim. Belg., *29*, 243 (1920).

[3] Miller, Bull. soc. chim. Belg., *43*, 279 (1934).

The intimate contact of liquid and vapor is perfectly assured in the plate columns used industrially. When these are operating under optimum conditions they accomplish extremely close fractionations.

An example of a dephlegmator of low efficiency, that unfortunately is still too widely used, is the Lebel-Henninger column. The returning liquid has to accumulate for some time in its side tubes, which function as siphons, before they empty themselves and return the liquid to the flask. The result is a jerky return, as well as an inadequate contact of the liquid and vapor. Consequently, the fractionation is poor and proceeds intermittently.

Some empirical rules often used in fractional distillation are:

(a) The less volatile compound is generally more easily recovered than the other. For example, in the fractionation of a mixture of equal weights of benzene and of toluene, Young, after the third pass, recovered 92% of the pure toluene, but only 22% of the benzene.[2]

(b) A separation that is difficult because of the proximity of the boiling points of the components of the mixture is made easier by operating under a reduced pressure. The difference in the boiling points then becomes greater. Francis [1] used this method successfully to separate normal and isopropyl bromides.

---

[1] Miller, Bull. soc. chim. Belg., *43*, 247 (1934); C. R. 15ième Congrès, Soc. Ch. Ind. Brussels, 1935.

[2] Young, *op. cit.*, p. 158.

(c) The separation of the more volatile component in the pure state is almost impossible if the boiling-point curve is nearly horizontal to the origin. This is often the case when the components are not miscible, even though their boiling points are quite different. For instance, the boiling point of isopentane (27.95°) is raised only 1.2° by the presence of 6.8% of nitrobenzene, even though the latter, under normal pressure, does not boil until the temperature reaches 211°.[2] This is also the reason why benzene is often contaminated with normal heptane (b.p. 98.4°). The boiling point of benzene (80.2°) is changed only 0.01° by the presence of 4% of heptane.[3]

(d) If the two components to be separated have boiling points near each other, it is often possible to accomplish an effective fractionation by including one of the components in an azeotropic mixture. For example, benzene (b.p. 80.2°) and cyclohexane (80.8°) cannot be separated by distillation, but if the benzene is in excess, it suffices to add a little methyl alcohol and the cyclohexane will distil completely as a binary mixture (b.p. 54.2°); the corresponding methyl alcohol-benzene mixture boils at 58.4°.

A similar method may be useful in dehydrating a liquid, which it is better not to subject to too high a temperature. Wuyts,[4] in the preparation of esters (*p*-toluenesulphonic acid as catalyst), eliminated the water, as soon as it was formed, as a binary mixture with excess alcohol. Atkins[1] dried sugars by dissolving them in absolute alcohol, then added some benzene, distilled off the ternary water-alcohol-benzene mixture, and then boiled off the alcohol, which left the sugar perfectly dry.

---

[1] Francis and Young, J. Chem. Soc., *73*, 920 (1898).

[2] Timmermans, Thesis, Brussels, 1911, p. 187.

[3] Timmermans, Bull. soc. chim. Belg., *29*, 227 (1920).

[4] Wuyts, Bull. soc. chim. Belg., *33*, 180 (1924).

Duclaux[2] separated acetone from the methyl alcohol, contained in wood spirit, by distilling in the presence of chloroform. The third component formed azeotropic mixtures with each of the other two compounds, and these mixtures, one positive, the other negative, have boiling points much farther apart than those of the two original components (53.5° and 64.7° as compared with 64.7° and 56.2°).

(e) If the existence of an azeotropic mixture makes the removal of a component impossible, the impurity may sometimes be eliminated as part of a ternary mixture. For example, ethyl alcohol cannot be dehydrated by a simple fractional distillation, because the alcohol and water form an azeotropic mixture (4.4% water), whose boiling point is too near that of pure alcohol. If benzene is added, all the water distils as part of a ternary mixture that can be separated easily from the excess of anhydrous alcohol.[3]

The boiling points are:

Ethyl alcohol	78.3°
Ethyl alcohol + water	78.15
Water + benzene	69.2
Alcohol + benzene	68.25
Ternary mixture	64.85

---

[1] Atkins and Wilson, J. Chem. Soc., *107*, 916 (1915).

[2] Lausenberg and Duclaux, Bull. soc. chim., [4] *29*, 135 (1921).

[3] Young and Fortey, J. Chem. Soc., *81*, 739 (1902).

To sum up, distillation is the most effective method of fractionation. One of its great advantages is that the various phases of the operation can be followed with a thermometer, even while the experiments are in progress. Such supervision is not nearly so feasible in fractionation by freezing, etc.

CHAPTER XIII

OTHER PHYSICAL METHODS OF PURIFICATION

These methods are quite varied. In addition to the usual procedures of fractionation, they employ electrolysis, adsorption, physical precipitation, etc. Their great advantage lies in the fact that no foreign matter is introduced into the material to be purified, or at least only such materials as are easily eliminated after they have served their purpose.

1. *Fractional solidification*

The theoretical bases of this process are identical with those of distillation. Much less study has been devoted to it than to distillation. It has the advantage that in many cases the components crystallize directly in the pure condition. However, the great difficulty in this procedure lies in separating the crystals completely from their mother liquors and inclusions. The filter presses used in industry do not seem superior in this respect to the methods of suction filtration customarily employed in the laboratory.

The writer has often used fractional fusion. The substance to be purified was completely solidified in a long-necked vessel immersed in a freezing bath, and prevented from separating in a single lump by stirring from time to time. The crystals were then placed in an elongated funnel, the mother liquors drained off as soon as they formed and their removal was hastened by pressing the crystals. It was very easy to follow constantly the rise of temperature with a thermometer placed among the crystals and to collect separately the successive fractions. When purifying materials having a relatively low heat of fusion, such as cyclohexane, the melting is too rapid, and in such instances it is necessary to surround the funnel with a muff that dips into a bath kept scarcely 1° above the melting point of the material being treated.

If two materials of similar properties are to be separated, it is possible sometimes to convert them into an intermediate product that will facilitate the complete separation of the two original components. The third component can then be eliminated chemically, and the other two recovered in a pure state. Urbain [1] made excellent use of this expedient to fractionate the rare earths. Example: Fractional crystallization of the nitrates of samarium and europium by adding bismuth nitrate, whose solubility is intermediate between that of the nitrates of the other two metals.

Although distillation is most often used for fractionation, fractional solidification can be recommended in the following special cases:

(a) to separate materials that form an azeotropic mixture. For instance, traces of benzene can be removed from cyclohexane only by fractional crystallization.

(b) to separate materials that lend themselves poorly to distillation because of their high boiling points or their instability. The separation of the higher fatty acids is an instance. The compounds to be separated may be transformed into more volatile compounds, in this case the esters, that are easy to distil.

---

[1] Urbain, J. chim. phys., *4*, 40 (1906).

(c) to separate materials whose boiling points are too close to each other. An example is furnished by position isomers, which generally do not form solid solutions with each other.

On the other hand, sometimes fractional crystallization must be avoided if possible, particularly if there is danger of the presence of isomorphic mixtures. Under these circumstances, the separation of the components generally entails great losses of the products in the form of irresolvable mixed crystals.

2. *Other changes of physical state*

In addition to the usual methods of fractionation, that are based on vaporization and crystallization, there is a series of procedures that utilize other changes of physical state to separate the components of a mixture.

Two materials having the same physical state (solid, liquid, gas) under the ordinary conditions of temperature and pressure, may sometimes easily be separated quantitatively by merely changing the temperature. Thus, the ammonium salts of volatile acids may be eliminated completely by calcination at temperatures at which many mineral compounds are still non-volatile and unchanged. Likewise, gases hard to liquefy are purified easily by freezing out all the impurities at a low temperature. This has been applied to helium, for instance.

Physical precipitation or "salting out" is useful in this respect, but the separation of the components is never complete. Raymond Lully (1235–1315), used this procedure to expel ethyl alcohol from its aqueous solutions; he saturated them with dry sodium carbonate. Similarly, small quantities of pyridine can be detected in ammoniacal solutions, by saturating them with ammonium sulfate which drives out the dissolved pyridine.[1] The fractional coagulation of certain colloids by addition of traces of electrolytes often makes it possible to separate these mixtures into their constituents. The fractional precipitation of albuminoids is a typical application of this procedure.

3. *Action of molecular forces* (e.g. adsorption, defecation)

The utilization of these forces often makes it possible to carry out purifications that seemingly cannot be accomplished by other means, as in the case of slightly volatile materials, turbid liquids, etc. To facilitate the action of the molecular forces, the material to be purified, either dissolved or in suspension, is put into intimate contact with a very finely divided or porous substance of great adsorbing powers, (charcoal, bone black, cocoanut charcoal, etc.). For instance, cloudy liquids are often clarified or decolorized by passing them through a layer of charcoal.

Sometimes a voluminous precipitate is produced within the liquid to be purified, and on settling it carries down all the suspended matter. The defecation of sugar liquors has this purpose. Spring[2] used this method to prepare optically empty liquids, in which all of the suspended particles were agglomerated with the aid of gelatinous hydrates.

Another, more rapid but less efficient, method of removing fine suspensions from liquids, fused materials and even from gases, is to use the sintered glass filters (Jena G_6) whose pores have a mean diameter of 1–1.5μ.

An analogous principle is employed for the absorption of the last traces of other gases from helium; cocoanut charcoal cooled in liquid air is used. This excellent method finds application in the manufacture of double walled vacuum flasks.

---

[1] Crismer, Bull. soc. chim., [3] *8*, 182 (1892); Ann. Soc. Med. Chir. de Liège, p. 183 (1891).

[2] Spring, Bull. Acad. roy. Belg. classe sci., p. 174 (1899);

Attention should be directed to the difficulty of eliminating the last traces of gas retained on the walls of glass vessels or occluded in metals even after prolonged evacuation and exposure to a high temperature. See the experimental studies of Sieverts,[1] Guichard,[2] and Germann.[3] The importance of this source of error is particularly apparent in the following example. The hydrogen retained by silver, that had been fused in an atmosphere of this gas as Stas recommended, had an indirect effect on the atomic weights of a large number of other elements, and caused errors as great as 1/2000 in the case of phosphorus.

The action of molecular forces is very unfavorable in the removal, by washing, of the last traces of the mother liquor from a colloidal precipitate. Often it is preferable, by suitable treatment, to transform the colloid into a crystallizable material that is easier to wash. For instance, hydrous cobalt oxide tenaciously retains potash, but after ignition the resulting anhydrous cobalt oxide is easily freed of alkali.[4]

Conversely, selective adsorption by suitable adsorbents is the basis of the chromatographic methods that permit the quantitative separation of compounds that are closely related in composition and properties.[5] For instance, the three isomeric carotenes, which differ only by the position of one double bond, can be separated by this column analysis. α carotene, dextrorotatory, is adsorbed by calcium hydroxide; β carotene, inactive, by calcium oxide; and γ carotene, also inactive, which constitutes only 1/1000 of the mixture, is retained by alumina.[1]

---

[1] Sieverts, Z. physik. Chem., *60,* 129 (1907).

[2] Guichard, Bull. soc. chim., [4] *11,* 49, 100 (1911).

[3] Guye and Germann, J. chim. phys., *14,* 195, 204 (1916).

[4] Dutoit and Grobet, J. chim. phys., *19,* 328 (1921). These authors pointed out a series of analogous observations in the separation of mixtures of salts of calcium and magnesium, and of calcium and barium.

[5] For a general discussion see: Schwab, Z. Elektrochem., *43,* 791, (1937); Zechmeister and Cholnoky, *Die chromatographische Adsorptionsmethoden.* Leipsic, 1938; *Physikalische Methoden der analytschen chemie,* vol. III, Leipsic, 1939.

4. *Electrolysis*

This process is used to separate certain metals from their soluble impurities. The separation is based on the differences of the solution tension of the various metals. When electrolyzed under proper conditions, only one of them is deposited. The separation is especially easy in three cases:

(a) if the metals are sufficiently distant from each other in the electrochemical series, the difference in their solution tensions is relatively great. The electrolysis conducted at a suitable voltage and amperage, and at a given temperature and concentration, will produce pure metal directly. Electrolytic copper, obtained in this way, has a purity of 99.99%.

(b) if the metals to be separated are, on the contrary, closely related from the electrolytic viewpoint, one of them can be bound into a compound furnishing a complex ion. The metal ion will be kept at such low concentration that the solubility product will not be reached in the presence of a precipitant. This facilitates the separation. Nickel determined in a solution of $(NH_4)_2Ni(SO_4)_2$ is an example.

(c) one of the metals may be treated so that it will separate at the anode in the form of an electronegative compound. For instance, lead can be thus deposited as the dioxide.

---

[1] Karrer and Walker, Helv. Chim. Act., *16*, 641 (1933).

CHAPTER XIV

ORDINARY PURIFICATION REAGENTS

These reagents are intended to remove the impurities most frequently encountered. These contaminants come from the surroundings or arise during the preparation, that is, from the air (oxygen, nitrogen, carbon dioxide, moisture), from the apparatus (silica, alkalies), or from the usual solvents (water, alcohol, ether, etc.).

1. *Drying agents*

Drying agents are the most common purifying reagents. They combine with water to form compounds exhibiting very low dissociation pressures; the lower this pressure, the more efficient the drying agent. However, when the vapor pressure of water in the surrounding medium has reached that produced by the dissociation of the hydrate it is impossible to push the dehydration further by increasing the quantity of drying agent. It follows that the introduction of a poor drying agent into a very dry medium, instead of improving the desiccation, merely introduces a fresh quantity of water, that comes from the traces of moisture that every drying agent carries with it.

The relative efficiency of a drying agent is therefore the same no matter what the medium to be dried, provided no secondary complication intervenes.

The drying power of a material is inversely proportional to the dissociation tension of its hydrates. Experiments by

Sidgwick[1] showed the relative efficacy of the more common drying agents. The measurements were made by putting benzene saturated with water into contact with the drying agents in such a way as to attain the desiccation equilibrium. This was assured by repeatedly drying the benzene with the particular desiccant until the freezing point remained unchanged. The following table demonstrates that the lowering of the freezing point, at equilibrium, varies approximately in the same order as the dissociation tension of the respective hydrates at 5.5°, the temperature of the experiments.

Desiccant	*Dissociation pressure of hydrates in mm. of Hg at 5.5°*	*Freezing temperature of benzene saturated with water (Sidgwick)*	*Milligrams of water per liter of air at 25° (Baxter)*	*Humidity of air at 20° (Obermiller)*
—	6.73 (pure water)	5.393°	22.75	100
Na_2SO_4	5.11	5.420	—	92
K_2CO_3	2.62	5.454	—	45
$CuSO_4$	0.74	5.482	1.4	—
$ZnCl_2$	0.67	—	0.8	—
$CaCl_2$	0.61	5.484	0.36	35
NaOH	0.11	5.491	0.16	—
H_2SO_4	—	—	0.003	—
KOH	—	—	0.002	8
P_2O_5	0	5.493	0.000	0

This table also includes the results of analogous studies of the drying powers of different substances as measured by other methods. For instance, Baxter[2] determined the number of milligrams of water remaining in a liter of air at 25°, after it had been dried with the usual drying agents. The smaller the quantity of residual moisture, the more active the drying agent. Obermiller[3] ranked these same materials by determining the degree of desiccation reached in a given mass of gas at 20°. Here too, the decreasing figures correspond to a more powerful drying action. Yoe [1] published a review of all the studies of this question.

---

[1] Sidgwick, J. Chem. Soc., *117*, 1340 (1920).

[2] Baxter and Starkweather, J. Am. Chem. Soc., *38*, 2038 (1916).

[3] Obermiller, Z. physik. Chem., *109*, 145 (1924).

The most active drying agent is phosphorus pentoxide. Morley [2] demonstrated this by showing that a current of moist air, dried by passage through a tube of adequate length charged with this desiccant, lost no more water when passed through a second tube containing this chemical. This was not the case if the air had been previously passed through the other drying agents. The dissociation pressure of metaphosphoric acid is practically nil up to 90°.[3] Phosphoric anhydride is usually appropriate for the drying of gases and of many organic liquids (hydrocarbons, halogenated derivatives, nitriles, ethers, fatty acids). Young showed that this compound is necessary to complete the drying of esters that already had been roughly dried by neutral sodium carbonate. Phosphorus pentoxide cannot be used to dry basic compounds (amines, ammonia, etc.), or unstable materials that easily lose water to form condensation compounds (acetone, etc.). The losses are less serious with ketones if their vapors are passed, under reduced pressure, through a tube containing powdered phosphorus pentoxide.[4]

Among the other drying agents, sodium, quick lime, barium hydroxide, and caustic potash are particularly indicated for basic compounds, alcohols, etc. Crismer [5] showed that sodium alone is suitable for methyl alcohol, and lime for the other alcohols. Barium oxide is recommended for the amines.

---

[1] Yoe, Chem. News, *130*, 340 (1925). See also Morton, *Laboratory Technique in Organic Chemistry*, New York, 1938.

[2] Morley, J. Am. Chem. Soc., *26*, 1171 (1904).

[3] Lacoss and Menzies, J. Am. Chem. Soc., *59*, 2471 (1937).

[4] Timmermans and Gillo, Roczniki Chem., *18*, 812 (1938).

[5] Crismer, Bull. soc. chim. Belg., *8*, 18 (1904).

The salts commonly used for drying purposes usually are not sufficiently active to dry liquids completely, but they are useful to remove the major part of the water, or to dry, as well as possible, unstable materials, such as acetone. However, magnesium perchlorate is just as effective as phosphorus pentoxide and has the advantage that it can be regenerated easily by heating it in a current of dry air.[1]

Sulfuric acid plays a role analogous to that of the salts in the preliminary drying of non-basic gases before bringing them into contact with phosphorus pentoxide.

2. *Other common impurities*

Certain other solvents may also be removed chemically by incorporating them in a crystalline addition compound. Calcium chloride can be used to remove alcohol from a mixture, sodium bisulfite will take out acetone, mercuric chloride will serve for ammonia and aliphatic amines (not pyridine), sulfuric acid and phosphorus pentoxide remove the alcohols, along with the water, from ether.

Carbon dioxide is easily retained by pellets of potassium hydroxide because dry potassium carbonate has a very low dissociation pressure at room temperatures. Air, and other dissolved or occluded gases ordinarily are more easily eliminated by purely physical methods.

If the products of the surface decomposition of glass must be avoided, the glass can be subjected to a rather prolonged treatment with steam, which dissolves all the soluble impurities. If these precautions are inadequate, vessels of quartz (to avoid alkalies) or of platinum (to avoid silica) can be used.

---

[1] Willard and Smith, J. Am. Chem. Soc., *44*, 2255 (1922); Smith, Brown, and Ross, Ind. Eng. Chem., *16*, 20 (1924).

CHAPTER XV

CHEMICAL CRITERIA OF PURITY

THE SENSITIVITY OF REAGENTS

AFTER a pure material has been obtained and subjected to a suitable method of fractionation, the various fractions must be shown to be identical by means of delicate criteria of purity. These tests may be chemical (reactions) or physical (constants).

A. *Sensitivity of reactions*

The sensitivity of a reaction is measured by the minimum quantity of a material that can be detected by its aid.

Example: the precipitate formed by the addition of a sulfide is a much more delicate test for traces of silver than that produced by chloride, because silver sulfide is much less soluble than silver chloride. (According to Treadwell, the solubility of the sulfide is 0.02 mg. per 100 gm. of solution, of the chloride 0.2 mg.) Consequently, hydrogen sulfide is a better test for detecting traces of silver, present as impurity in a solution, than hydrochloric acid.

However, certain factors influence the sensitivity of a reaction:

(1) The sensitivity is never infinite, because an excess of reagent, no matter how small, is always necessary to produce the desired effect, such as a color change or a precipitate that is never absolutely insoluble.

(2) The sensitivity of the reaction varies with the conditions of the medium.

For instance, the precipitation of the ions of heavy metals by alkalies is hindered by the presence of many hydroxylated organic compounds that form complex ions (with cobalt, nickel, manganese, etc.) and thus exert a stabilizing influence that prevents the precipitation by the alkalies.

(3) A reaction, although quite delicate, may not be rapid.

For example, silver salts immediately form a precipitate with the iodide ion, but their reaction with the iodine of alkyl iodides is very slow.

The precipitate is sometimes slow in appearing in extremely sensitive reactions. This is generally the case when precipitation is made from very dilute solutions (e.g. ammonium phosphomolybdate).

(4) A reaction, no matter how delicate, is not always perfectly specific.

For instance, many color changes are group reactions (e.g. phenols + ferric chloride). It is then necessary to apply several different tests to confirm the result.

(5) It is often possible to increase the delicacy of a reaction by indirect methods.

Examples are: the detection of very fine precipitates by means of the Richards nephelometer;[1] measurements of the changes in electrical conductivity with the progressive addition of a reagent in place of observing color changes;[2] concentration of a colored material in a small volume of solvent in which it is very soluble (e.g. ferric sulfocyanate or perchromic acid in ether).

---

[1] Richards and Wells, Am. Chem. J., *31*, 235 (1904).

[2] Dutoit, J. chim. phys., *8*, 12 (1910).

The most sensitive chemical reactions are: the formation of so-called insoluble precipitates, color changes, biological reactions.

B. *Slightly soluble precipitates*

All salts are slightly soluble. If their saturated solutions are very dilute, it may be assumed that the ionic dissociation is complete, and the concentration may be calculated from the conductivity.

SOLUBILITY OF SALTS

Salt	*Equivalents per liter of saturated solution at 25°*	*Solubility Product at 25°*
AgCl	1.4×10^{-5}	2.0×10^{-10}
AgBr	6.6×10^{-7}	4.35×10^{-13}
AgI	1.0×10^{-8}	1.0×10^{-16}
Ag_2S	1.1×10^{-8}	1.33×10^{-24}
$PbSO_4$	1.5×10^{-4}	2.2×10^{-8}
$BaSO_4$	2.0×10^{-7}	4.0×10^{-14}
MnS	2.7×10^{-8}	7.0×10^{-16}
CdS	2.7×10^{-14}	7.0×10^{-28}

Theory of the solubility product (SP)

In the saturated solution of a salt *AB* in contact with its solid phase there is an equilibrium between the active solid phase (c_s) and the dissolved unionized salt (c_d), and between the latter and its ions:

$$k_1 = \frac{c}{c_s}; \; k_2 = \frac{c_{A^+} \times c_{B^-}}{c_d}.$$

Since the active mass of the solid is constant (at constant temperature), c_d is also constant, and consequently the product ($c_{A^+} \times c_{B^-} = \text{S.P.}$) of the ionic concentrations is likewise constant. This so-called solubility product, invariant at a given temperature, fixes the concentration of the dissolved salt and hence the delicacy of the precipitation reaction, and vice versa.

For instance, an excess of precipitating agent ($BaCl_2$) favors the precipitation of barium sulfate because if the concentration of the barium ion rises that of the sulfate ion must decrease, with the result that more barium sulfate precipitates.

The sensitivity of silver salts toward hydrogen sulfide is diminished greatly by adding potassium cyanide. A complex anion $[Ag(CN)_2]^-$ is formed, and this is so stable that very few silver ions remain in the solution. Consequently, a very large excess of hydrogen sulfide is necessary before the solubility product of silver sulfide is reached.

C. *Indicators*

These are electrolytes whose color differs according to the acidity or alkalinity of the medium. They serve especially for determining neutrality, more or less exactly, when titrating acids and bases.

A good indicator ought to be both *delicate,* that is, change sharply in color with a slight variation in the state of the medium, and *exact,* that is, its color change should coincide as closely as possible with the completion of the chemical change to be observed.

According to Hantzsch's theory, acidimetric indicators are weak acids or bases whose molecule (HA in the case of acids) is in equilibrium in part with its ions (A^-, H^+) and in part with a tautomeric, non-dissociable form (AH). The latter has a color different from that of the ionizable form, and the concentrations of the three species of particles are related to each other and to the concentration of the ions H^+ and OH^- of water by the three equilibrium relations:

$$K_1 = \frac{(HA)}{(AH)},\ K_2 = \frac{(H^+)(A^-)}{(HA)},\ K_{\mathrm{H_2O}} = (\mathrm{H}^+)(\mathrm{OH}^-).$$

The equilibrium between the two tautomeric forms of the indicator finally depends then on the acidity of the solution. An appreciable quantity of the non-dissociable form can exist only if the concentration of H^+ is sufficiently high, and the color change will not occur unless this concentration is reached.

The delicacy of the color changes is especially favored if the two colors shown by the indicator are quite different, and if the passage from one to the other is sharp, or if one of the forms of the indicator is colorless. From this point of view, phenolphthalein is ideal, with its non-dissociable, colorless molecule and its red ion. However, this is not the only point to consider.

The salts of strong bases and acids are not appreciably hydrolyzed. Therefore, the neutralization of a strong base by a strong acid, or vice versa, produces a solution containing equal concentrations of H^+ and OH^-, that is, the solution is neutral, like pure water. Since the indicator is a weak acid or base, the slightest excess of strong acid or base will suffice to produce the color change. Under such circumstances, the indicator is quite sensitive and accordingly titration should be made with a strong acid or base.

When dealing, however, with salts derived from weak acids or bases, the hydrolysis in aqueous solution is considerable. The solution will be acid or basic, and at the equivalence point will show the reaction of the stronger constituent. If an indicator is to yield correct results under these conditions, its color changes must occur exactly at the hydrogen ion concentration corresponding to that existing in the aqueous solution of the hydrolyzable salt produced by the titration.

The concentration of H^+ ordinarily varies only from 1 to 10^{-14}. In pure water it is 10^{-7}. Its value at the transition point of several ordinary indicators is:

methyl orange	10^{-4}	$pH = 4$
litmus	10^{-6}	$= 6$
phenolphthalein	10^{-8}	$= 8$

Litmus and phenolphthalein are both suitable for titrations of strong acids and strong bases. Phenolphthalein, a weak acid, is excellent also for the titration of weak acids by strong bases (and vice versa) producing salts that hydrolyze to give an alkaline reaction. Methyl orange acts as a weak base, and is suitable for the titration of weak bases by strong acids (and vice versa) producing salts that hydrolyze to give an acid reaction.

D. *Biological reagents*

The nature and sensitivity of these reagents is quite varied. Sometimes they are more delicate than all other tests. For instance, a fragment of musk can scent a large area for a long time and yet lose no appreciable weight.

In physiological experiments on animals, it has been shown that certain organs react to a solution containing only one five-millionth of adrenaline. According to Kögl,[1] a certain vegetable hormone, biotin, that can be extracted from yeast, still affects the growth of plants at a concentration of 1 in 400 billion.

---

[1] Kögl, Comptes rendus du VIth Congrès de Chimie Solvay, Brussels 1937, p. 433.

In the preparation of bacteriological culture media, it is often indispensable to prescribe sugars corresponding to a well-defined stereochemical structure. Certain types of microorganisms are incapable of feeding on a substitute sugar, even though it is the optical antipode of their usual nutriment.

CHAPTER XVI

PHYSICAL CRITERIA OF PURITY

A. *General considerations*

THE study of physical constants furnishes valuable criteria of purity since such measurements make it possible to compare quantitatively the different fractions of a single preparation or of different lots of the same material.

The purity of a substance is an entirely relative concept, and in each case it is necessary to appraise properly the effect of the presence of harmful impurities on the sensitivity of the tests employed to discover the purity of the sample, and to evaluate the precision with which the selected constants can be determined.

From this follows the rule: one of the criteria of purity, imposed by practical experience, is always none other than the constant that is to be determined. The sample studied is pure only if, from sample to sample or from fraction to fraction, the variation in this constant is not greater than the limits of precision to be attained in the final measurement. Otherwise, the test loses all significance. For instance, the density of pure acetone is especially affected by the presence of moisture. Consequently, any sample of acetone whose density does not vary may be considered as sufficiently dried. But such acetone may be quite impure with respect to its specific conductivity, which is quite susceptible to traces of dissolved salts but is not appreciably influenced by the presence of a little water.

The use of a single criterion of purity may lead sometimes to the supposition that a sample is pure when in reality it is a mixture (eutectic, azeotropic). The use of a second criterion is imperative in every case. The choice of this second test will be dictated by a consideration of the most harmful impurities, as well as by the simplicity of the methods to be used. For example, the azeotropic mixture of alcohol and water simulates, by the constancy of its boiling point, a pure material, even though it contains 4.4% water. Furthermore, its boiling point (78.15° under normal pressure) is exceedingly close to that of anhydrous alcohol (78.3°). However, by measuring the densities, or preferably the critical solution temperatures in gasoline, the azeotropic mixture can be distinguished easily from pure alcohol, because their critical solution temperatures differ by 52°.

The principal criteria of purity can be divided into two classes:

(1) those corresponding to heterogeneous equilibrium constants (boiling point, freezing point, critical temperature, etc.);

(2) those in which the constants of homogeneous systems are studied (density, index of refraction, spectrum, conductivity, speed of reaction, etc.).

B. *Heterogeneous equilibrium constants*

(1) *Freezing point:* This has been used as a means of identification since 1832 or earlier. When determined in a capillary tube the result is not highly precise, but in a freezing point apparatus with little super-cooling and observation of the freezing break on the cooling curve, this constant can be measured, without difficulty, with an ac-

curacy close to 1/100th of a degree.[1] If the material tends to decompose on melting, it is better to use the method of instantaneous fusion described on p. 26.

If the solidification temperature of the liquid is to be determined, rather than the melting point of the crystals, the influence of dissolved gases (air, water vapor, carbon dioxide) must be kept in mind. They can be removed by prolonged boiling and by allowing the crystallization to take place in vacuo.[2] The crystals thus obtained are allowed to melt slowly, the liquid permitted to drain away, and then the crystals give exactly the solidification temperature. This method is also used to determine the zero point in thermometry.

Sometimes a secondary reaction between a molten metal and the air may lead to serious errors, unless sufficient precautions are taken. Copper melts at 1083° in a vacuum, but in the presence of air this point falls to 1064° (eutectic, $Cu + Cu_2O$).

(2) *Boiling point:* Young showed that it is possible to obtain without insurmountable difficulties, even among organic compounds, pure materials whose boiling point remains constant (within $\pm 0.01°$) during the entire fractionation. To maintain this constancy, it is necessary to boil the pure material neither too violently nor too slowly. Otherwise, the liquid-vapor equilibrium is not attained in contact with the bulb of the thermometer. A mean rate of distillation of one drop of liquid per second is particularly recommended.

Swietoslawski[3] has introduced an ingenious method for testing the homogeneity of liquids, by determining the boiling point with the aid of his ebulliometers. These instruments make possible a comparison of the boiling temperature of the liquid residue with that of the condensed vapor with which it is in equilibrium. This difference (Δt) can be measured easily within 0.001°, so that the variations in the properties of a liquid can be followed with great precision throughout the whole fractionation. He has proposed the following scale of purity for liquids:

---

[1] Landolt, Z. physik. Chem., *4*, 349 (1889).

[2] Meyer, Z. physik. Chem., *90*, 721 (1915).

[3] Swietoslawski, *Ebulliometry*, revised edition, New York, 1937.

Degree of Purity	Δt *observed*
I	1.00° to 0.10°
II	0.10° " 0.05°
III	0.05° " 0.02°
IV	0.02° " 0.005°
V	0.005° " 0.000°.

The vapor pressure of a pure liquid, like its boiling point, should remain absolutely constant, at a constant temperature, throughout its vaporization or condensation. This test of purity is seldom used because it does not indicate whether the impurity is a second more volatile component, or simply traces of dissolved air.[1] However, its very great delicacy is a decided asset of this test.

The critical constants, critical temperature and pressure in particular, also vary tremendously if traces of impurities are present. Therefore, Altschul[2] proposed them as criteria of purity. However, for this purpose, they have been replaced easily by the critical solution temperature, which has great sensitivity coupled with a simple, elegant experimental procedure.[3]

---

[1] Young, J. chim. phys., *4*, 425 (1906); Sci. Pro. Royal Dublin Soc., [2] *11*, 89 (1906).

[2] Pictet and Altschul, Z. physik. Chem., *16*, 26 (1895).

[3] Crismer, Bull. assoc. belg. Chim., *9*, 145 (1895).

(3) *Solubility:* This is seldom used as a test of purity, except in the form of the critical solution temperature, whose systematic employment, introduced by Crismer, can be recommended highly.

The sensitivity of this constant to impurities may be extreme, but it varies with the relative solubility of the impurity in the two liquid phases in equilibrium at the critical solution temperature (Schreinemakers). For instance, a phenol-water mixture, whose critical solution temperature was 65.3°, showed the following changes in this temperature on the addition of 0.1 mole % of impurity:[1] naphthalene +7.1°; potassium chloride +8.3°; mercuric cyanide −4.2°; succinic acid −7.2°.

Cohen [2] showed that the solubility of salicylic acid in benzene, at 25°, changes enormously in the presence of traces of moisture: the solubility, at 30°, increases 10% if 1/3000th of water is added to the dry benzene.

4. *Speed of crystallization:* A substance crystallizes with greater difficulty as its purity decreases, and its rate of crystallization, measured at a given temperature, rises very rapidly as the purification advances. Michel [3] showed that 1/50,000 of water can be detected thus in methyl alcohol.

C. Other physical constants

(1) *Density:* This can be determined easily within 1/10,000th, which, for the usual liquids, corresponds to an error of 0.1° in the temperature. Consequently, it is preferable simply to make the measurements at 0°, in melting ice, thus avoiding all error of this magnitude. The results obtained under these conditions by various workers agree

---

[1] Timmermans, Z. physik. Chem., *58*, 129 (1907).

[2] Cohen and Dobbenburgh, Z. physik. Chem., *118A*, 37, (1925); Cohen and Miyake, *ibid.*, *119A*, 247 (1926).

[3] Michel, Bull. soc. chim. Belg., *48*, 149 (1939).

within this range. For instance, ether at 15° has a density of 0.71930,[1] 0.71919 (Wade),[2] and 0.71925 (Young).[3] It is easy to determine the density of liquids to within 1/100,000th by the comparative method of Smith and Wojciechowski.[4]

(2) *Index of refraction:* This can be measured easily to within 1/10,000th if the temperature is known to within 0.1°. However, this constant is not often used as a test of purity because the indices of the most common liquids differ by not more than several tenths. This greatly diminishes the sensitivity of this constant to impurities. See however Andrews' studies on the refractive index of absolute alcohol.[5]

(3) *Specific heat:* The latent heat of fusion of a pure liquid ought to be measured at constant temperature. After the liquid has crystallized completely at this temperature, the solid mass cools regularly and the value of the specific heat of the crystals ought to decrease more and more, conforming to a linear function of the temperature. If the substance is not ideally pure, the end of the crystallization occurs at a temperature a little below that at the beginning of the solidification. From that point, during the measurement, a part of the latent heat of solidification is added to the real specific heat of the crystals and this results in too high values of the apparent specific heat. Skau [6] showed that this criterion of purity is so delicate that no one has been able to prepare a solid, not even ice,[7] that passes this test perfectly.

[1] Taylor and Smith, J. Am. Chem. Soc., *44*, 2456 (1922).

[2] Wade and Finnemore, J. Chem. Soc., *95*, 1842 (1909).

[3] Ramsay and Young, Phil. Trans., *178*, 57 (1887).

[4] Smith and Wojciechowski, Roczniki Chem., *16*, 104 (1936).

[5] Andrews, J. Am. Chem. Soc., *30*, 353 (1908).

[6] Skau, J. Am. Chem. Soc., *57*, 243 (1935).

[7] Dickinson and Osborne, Bureau Standards, Bull., *12*, 49, (1915).

The specific heat of a crystalline phase ought, according to Skau,[1] always to be less than that of the corresponding liquid, if the sample being examined is sufficiently pure. It must be pointed out that this excellent criterion of purity is not applicable to organic materials with a low heat of fusion, in which the molecules still retain a certain degree of freedom within the crystalline network, and then the specific heat is of the same magnitude for the crystals as for the liquid.[2]

(4) *Flame spectrum:* This is exceedingly delicate, as shown by the difficulties encountered by Stas when preparing silver salts that would not also give the sodium lines.[3] This test was used by Hartley, then by de Grammont [4] to demonstrate the wide-spread distribution of traces of certain metals in nature.

(5) *Specific conductivity:* This has been employed particularly by Walden.[5] For example, four fractions of a sample of formamide that appeared to be homogeneous had, at 25°, specific conductivities of 210, 85, 25, 4.7×10^5. Only the last of these was really pure, with respect to its solvent properties.

---

[1] Skau, Bull. soc. chim. Belg., *43*, 287 (1937).

[2] Timmermans, J. chim. phys., *35*, 331 (1938).

[3] Stas, *Oeuvres complètes*, vol. 3, p. 202, 1894.

[4] de Grammont, J. chim. phys., *14*, 336 (1916).

[5] Walden, Z. physik. Chem., *46*, 144 (1903).

PART III

DETERMINATION OF PHYSICAL CONSTANTS

CHAPTER XVII

THE PRECISE AND ACCURATE MEASUREMENT OF A CONSTANT

ANY complete discussion of this topic requires the successive consideration of the following points:

(a) definition of the quantity to be measured;

(b) exact delimitation of the field of application of the particular constant;

(c) choice of a reference system or of units.

Precise definition of physico-chemical constants. This definition emanates from a formula connecting the different variables to be considered, that correspond to the forces involved in the phenomenon. The following constants illustrate this.

Density or *specific mass.* Two bodies attract each other inversely as square of the distance (l) that separates them and directly as the product of their masses (m', m''):

$$A = \frac{m'm''}{l^2}.$$

The mass is proportional to the volume if specimens of the same material are considered, but for different substances this is no longer true. The mass of each body is proportional not only to its volume (v) but also to a factor characteristic of the substance, namely its density or specific mass (d):

$$m = v \times d.$$

Density is therefore the mass of a unit volume.

Dielectric constant. Coulomb's law states that the attraction (F) between two charges or electric masses (c) of opposite sign can be represented by an analogous expression:

$$F = \frac{c'c''}{l^2}.$$

The electric charges are absolutely independent of the nature of the body on which they reside, but the intensity of the attraction between them varies as a function of the nature of the medium which separates the two charged bodies. The complete formula is then:

$$F = \frac{c'c''}{l^2} \times \mu,$$

in which μ is a proportionality factor called the dielectric constant of the particular medium.

A consideration of these formulae applying to two rather simple cases suffices to show how a precise definition of these two physical constants is obtained. Their exact value in each instance results from the application of a rigorous formula to well-defined physical magnitudes, and no ambiguity is possible. However, it is imperative that the definition not merely imply (as is often the case for μ in Coulomb's law) but, on the contrary, reveal all the factors that affect the value of the constant under consideration.

The same physical property may be expressed by quite different magnitudes, if a different constant is chosen to represent the property. For instance, instead of measuring densities, their reciprocals, namely, specific volumes, may be determined. In many electrical phenomena, it makes no difference whether electrostatic or electromagnetic units are used, because the values expressed in one system can be easily converted into those of the other by applying a proportionality factor equal to the speed of light in a vacuum. Either surface tension (α) or the capillary constant (a) may be used, since they are related:

$$a^2 = \frac{2\alpha}{d}.$$

Extensive and *intensive properties.* It is essential to distinguish two classes of physical magnitudes, which differ not only intrinsically, but also in the methods by which they are measured, and in their reciprocal relation.

Extensive properties are physical magnitudes whose nature is such that different fractions of the same kind can be added algebraically. They may cancel each other, but they can never become negative; their numerical value indicates how many times they contain the chosen unit. For example, two lengths may be added by placing them end to end; the total length equals the sum of its constituent parts. The length representing the distance between two points may decrease to zero, but a negative length is inconceivable. A length of three meters indicates that it can be divided into three fractions each equal to the meter, that has been chosen as the unit of comparison. The same holds for volume, mass, angles, quantities of electricity and heat, etc., all of which are known as quantity factors.

Intensive properties, on the contrary, cannot be added to each other nor can they cancel each other. They are distributed along a conventional scale and consequently can become negative. Only the difference between two points on this scale can be measured; a difference which itself is an extensive quantity.

For instance, different temperatures may be arranged in a series, each term being higher than the preceding one and lower than the one coming after. The temperatures of two bodies may be equal; if different they may be ranked with respect to each other, notably by comparing them with conventional fixed points. Certain temperatures measured on the ordinary scales have a negative value. If two bodies are placed in contact, the temperature of the whole mass will not be equal to the sum of the original temperatures but to their mean, their respective masses and specific heats being taken into account. It is possible to determine the difference between two points on the scale by measuring, for instance, the quantity of heat necessary to raise the temperature of one gram of a given substance one degree, or by the change in volume of a thermometric substance, etc. Thus temperature, like time, intensity of a sound, difference in level of a water fall, potential of discharge, etc., is an intensity factor.

Field of application. If measurements are to be without ambiguity, it is essential not only to define the physical quantity precisely, but also to indicate, with the greatest care, the value of all the factors that may influence the constant to be determined. Consequently, in the majority of cases, it is essential to know in full detail the physico-chemical constitution of the system under consideration. Therefore, since systems like the following do not comply with these conditions, the study of the so-called "constants" of loosely defined materials, such as gasoline, alloys, wood, milk, etc., that are so important from a practical standpoint, is of little interest in a discussion of the present type.

It is also necessary to specify all the physical determinants that are capable of influencing this or that constant.

First of all, the physical state of the substance (gas, liquid, solid, allotropic or polymorphic varieties) must be known; and then the thermodynamic variables (tensor properties) of the system (temperature, pressure, concentration). In considering the latter, especially in the study of solid systems, the possibility of hysteresis must never be forgotten. This causes the system to retain properties corresponding to thermodynamic variables other than those existing at the time the measurement is made. In many cases, it is also necessary to indicate any vectorial properties (e.g. crystalline parameters, preferential direction of smegmatic liquids).

Certain physical constants can be classed together in two categories, subordinated to each other:

(a) The first includes those which the writer calls *characteristics of state,* which define numerically the regions of existence of the different physical states of a system and the conditions of their heterogeneous equilibria. Examples are: critical temperature, fusion- and transformation-curve, pressure of saturated vapor, solubility curve, etc. A precise knowledge of these constants requires no complementary information.

(b) The second category includes all the other stoichiometric constants, such as density, viscosity, index of refraction, etc., whose values vary with the physical state and change sharply on passing from one phase to another, even though the sample is a single substance that chemically remains the same in the new phase.

CHAPTER XVIII

UNITS, STANDARDS AND FIXED POINTS

After a physical quantity has been defined unequivocally, it can be represented by a numerical value if it has been measured by comparing it with a quantity of the same kind that has been chosen as unit.

At first sight, there seem to be certain physical quantities that are independent of the choice of units, such as the index of refraction and the dielectric constant. This is only apparently so because these properties are not expressed as absolute quantities; they are merely simple ratios in which an obvious unit is implied. Thus, the index of refraction is by definition the ratio of the speed of light in the substance being examined and *in vacuo;* since this latter quantity is taken to be equal to unity it seemingly drops out.

Choice of units from a theoretical viewpoint. This choice has been made in accordance with quite varied principles, and the evolution that has occurred in this field may be reviewed in three main stages:

(a) *Primitive stage.* In the beginning, units were chosen arbitrarily to meet the immediate practical needs. They were entirely independent of each other because they were separately defined for each type of measurement.

The pace, an old unit of topographic length, was independent of the ell, the unit used for the measurement of cloth. Even today in the British Isles, United States, etc., the yard and the gallon are used commercially though no rational relation has been established between these units. There are also isolated parts of physics where, for lack of anything better, units of this type have been adopted. The photometric unit proposed in 1884 by Violle is an example: it is the quantity of light emitted perpendicularly to its surface by a square centimeter of platinum, maintained at its solidification temperature.[1] The measurement of pressures in millimeters of mercury at 0° instead of in baryes (dynes/sq. cm.) is also entirely arbitrary.

(b) *Present stage.* This period is characterized by the adoption of coherent systems of units. The progress of physics brought to light certain necessary relations between the different physical quantities. From that time on only a relatively small number of fundamental units were arbitrarily defined, and the secondary units were necessarily derived from them.

In the system of electrical units, for example, the units of resistance (ohm), of electromotive force (volt), and current intensity (ampere), are so chosen that after two of them are fixed the value of the third necessarily follows. Actually, these units have been defined to satisfy the fundamental equation that had been found experimentally:

$$R = K \times \frac{E}{I},$$

in which K, a proportionality factor, equals unity.

Modern science uses several systems of units concurrently:

The *metric system* for geometrical, gravimetric, monetary units, etc.;

---

[1] Violle, Commission intern: Unités électriques. Paris 1884.

The *c.g.s. system,* which is applied to a great number of physical units of mass, force, velocity, etc.;

The *system of electrical units,* derived from the c.g.s. system.

(c) *Future stage.* The outlines of a new system of units that will be both universal and absolute are taking shape. There now exist as many systems of units as there are forms of energy (mechanical, electrical, heat units, etc.). Since these are only different expressions of a single fundamental quantity, and since their relative values are known, it will be more logical to refer all these systems to a few irreducible determinants. Then it will be possible to express all the other physical quantities in terms of these. Six fundamental parameters or determinants will suffice. They will be, for instance, the units of length, time, mass or force, temperature, dielectric constant and magnetic permeability. These will constitute a system of universal units.

Furthermore, up to the present, the units have been chosen as functions of the properties of selected substances. The unit of mass is the mass of a certain volume of water, the unit of electrical resistance is the resistance of a certain column of mercury, and so forth. It would be better if the universal units were also absolute units, entirely independent of the material being examined. The speed of light in a vacuum, the two radiation constants deduced from Planck's law, the constants of gravitation and of electric and magnetic fields, might be chosen. An entirely logical system of units, both universal and absolute, would be thus obtained, and only practical considerations should prevent its immediate adoption.

Choice of units from the practical point of view. After the units have been defined theoretically, the next step is to make them available in the form of practical metrological units.

Multiples or sub-multiples of the theoretical unit are often better suited to daily use, and the rules governing their choice are worthy of consideration. Which of the unlimited number of multiples or sub-multiples of the unit is best suited for practical purposes? Ought it coincide with the traditional unit still in use (the meter approximates the yard; the ohm, which equals 10^9 c.g.s. units, does not differ greatly from the Siemens unit)? Or should it be so chosen that the numbers encountered in daily practice are not too large or too small? The Ångström (one thousandth of a micron) is suitable for measurements of wave lengths; the light year for astronomical distances.

Standards and Points of Reference. After the practical unit is chosen it must be reproduced physically by a *standard.* Formerly, the standard was defined as the *material realization* of a natural constant. For instance, the meter was considered as equal to 1/40,000,000 of the earth's circumference, and the kilogram was taken as the mass of a liter of water at its maximum density, measured at sea level and at 45° of latitude.

This method of definition has the great disadvantage that each advance in the science of measurement makes necessary a slight correction in the unit, and consequently its absolute value changes a little. For example, the standard kilogram of the Bureau of Weights and Measures at Sèvres is known to be about 1/10,000th heavier than it should be according to the foregoing definition. The discovery of heavy water has both complicated and simplified this question. It has been complicated because the mass of a liter of water varies with the percentage of heavy water. It is simplified because the theoretical value of the kilogram can be made to coincide with that of the practical standard of Sèvres, by agreeing with MacLennan's proposal,[1] that the kilogram be defined as the mass of a liter of water containing the necessary percentage of heavy water.

The inconvenience of this continual inconstancy of standards can be avoided by the adoption of Guillaume's [2] proposal that the standard be defined not as the *realization* but only as the *material representation* of a unit. Instances are the standard meter of Sèvres, the standard helium thermometer in use at the Cryogenic Laboratory at Leyden, the standard ohms constructed by the principal Bureaus of Weights and Measures, etc.

Although the role of the material standards is thus reduced to some extent, their construction and application remain no less delicate because the constancy of the standard instrument must be ensured. A good standard ought to be subject to no variations, except those due to external variables that can be controlled easily and measured. For instance, glass is not suitable for the construction of a standard of length because of its hysteresis of expansion. There could be no certainty that after exposure to different temperatures it would always regain exactly the same length on its return to the temperature at which it had been calibrated originally.

The absolute fixity of material standards can never be guaranteed. Furthermore, if exclusive dependence is put on them, the possibility of their destruction constitutes a great danger. Such a disaster would make any new, exact evaluation of their absolute magnitudes impossible and would introduce uncertainty in the interpretation of the results of earlier measurements that had been expressed in terms of the lost standard.

---

[1] MacLennan, Proc. verbaux, Séances du Comité international des Poids et Mesures, [2] *18*, 3 (1937).

[2] Guillaume, *Unites et Etalons*, p. 48, Paris 1893.

These inconveniences can be avoided by comparing the value of a given standard with a physical constant that is characteristic of some substance under well-defined experimental conditions. This is why the experiments of Michelson are of such fundamental importance. He compared the length of the standard meter with the wave length of a given monochromatic light. The fixing of fundamental thermometric reference points, etc., is of like significance.

The construction of standards and their calibration as a function of physico-chemical reference points is also of great importance with respect to the secondary units. The quantitative relation of the secondary unit to the fundamental unit from which it is derived is not always known with a precision equivalent to that which can be obtained in the measurement of the physical quantity represented by the secondary unit.

For example, the mechanical equivalent of heat has not yet been determined with an accuracy as great as is actually attained in calorimetric measurements. Hence it is imperative to determine quantities of heat in terms of a calorimetric standard and not of a mechanical unit. This is the only means of not affecting all calorimetric measurements with the coefficient of inexactitude that still resides in the present accepted value of the mechanical equivalent of heat.[1]

Another case in which the use of physico-chemical reference points for the calibration of apparatus is always indicated arises when the exact reproduction of the standard apparatus is particularly delicate. Hence, for instance, the tremendous value of secondary thermometric fixed points in the calibration of mercury and resistance thermometers. The same holds for the preparation of carefully studied bases of reference when measuring quantities whose evaluation is as delicate as that of viscosity or the dielectric constant, for example.

---

[1] The Comité international des Poids et Mesures has adopted the relation: 1 calorie (15°) = 4.186 joules.

CHAPTER XIX

APPROXIMATION OF EXPERIMENTAL MEASUREMENTS

ALL measurements contain some error; absolute accuracy cannot be attained experimentally. This may be due to the effect of three types of causes acting concurrently.

(a) First of all, there is an excellent chance that the quantity to be evaluated and the unit which is to serve for the measurement may be incommensurable. *A priori*, this situation obviously makes an absolutely exact measurement impossible. For instance, the circumference and the radius of a circle are incommensurable; the weight of an object practically never is equal to an exact multiple (whole or fractional) of the gram, etc.

(b) The sensitivity of the measuring equipment, which must be used, is always limited. The value sought can be shown to be intermediate between two limits, one higher and one lower, but these never coincide.

Basic theory attributes unlimited sensitivity to certain instruments, but this is merely an illusion. In truth, this theoretical conclusion has been reached by accepting premises that are only approximately exact. These assumptions do not take account of the disturbing action of factors that may be neglected in ordinary practice, but whose importance increases as the measurement becomes more and more refined.

For example, the underlying theory of the balance states that the sensitivity of this instrument depends essentially on the distance between the center of gravity of the beam and its center of suspension. These points may be brought closer and closer until they coincide. It might be concluded that an unlimited sensitivity can be attained under this last condition, but this would be a grave error of judgment because no account would then be taken of the fact that the theory disregards friction. This is inevitable at the knife edge of the beam and obviously affects the sensitivity of the balance quite unfavorably. Here is a typical example of the danger resulting from the improper use of mathematical formulae without previous careful delimitation of the actual field to which they apply.

(c) The errors arising from the imperfection of the senses of the observer must also be taken into consideration. His organs, after all, are only instruments of the same kind as those used in the laboratory, and share their defects.

Various causes of the inaccuracy of measurements. These are subject to three kinds of errors:

(a) *Accidents.* These are grave or wild mistakes due to distractions or to the ineptitude of the observer. A mature worker in full possession of his resources is practically never guilty of these. Unfortunately, such accidents are always possible, even to a skilled observer, but they can always be easily discovered because they lead to grossly erroneous results.

(b) *Fortuitous errors.* These, in contrast to accidents, are generally quite slight, but are inevitable, because they arise directly from the lack of sensitivity of the observer's senses and his instruments. They can be recognized because they are distributed equally on each side of the mean.

(c) *Systematic errors.* These always occur in the same direction and remain of the same order of magnitude. They are due to an inherent fault in the experimental method employed or to a defect of the instrument.

For instance, an error in recording the weights on one of the pans of a balance should be considered an accident. The slight divergences observed on repeating the same weighing several times, under similar conditions, are fortuitous errors. The error introduced by an inequality in the length of the two arms of the beam would be a typical systematic error.

The correction of systematic errors may be accomplished, more or less completely, in different ways:

(a) By correcting the data furnished by the defective instrument, either by making a rational application of its theory, or by comparing the information it furnishes with that given by a standard instrument, or by calibrating the instrument with the aid of suitable reference points or standard materials. For example, when constructing a table of corrections for a thermometer, the stem of the instrument may be calibrated, or its readings may be compared with those of a verified thermometer placed in the same surroundings, or a record may be made of the temperature indicated by the instrument when it is used to measure the temperature of certain perfectly known fixed points.

(b) By employing a procedure which eliminates, as much as possible, the influence of the imperfections of the instruments. The method of transposition and compensation, such as the method of double weighings, is an example. The quotient method in which the value sought is given by the relation of two measurements both containing the same proportional error is another. This is used in the determination of the density, where the weights of a certain volume of the liquid and of the same volume of water are determined on the same pan of the balance, thus eliminating all effect of the possible dissymmetry of the beam. This also illustrates one of the great advantages of the differential methods, which give accurately the interval between the quantity being measured and a determined fixed point, and in which it is not necessary to verify beforehand the absolute value of the latter. This is also the method perfected by Smith and Wojciechowski[1] to measure the difference in the densities of two liquids by means of twin picnometers.

Causes of fortuitous errors.

(a) *Variation in sensitivity or accuracy of instruments.* These are due to slight changes in the conditions of the medium or to variations in the method of using the instruments. Consequently, the magnitude of these errors can be diminished, though they can never be completely eliminated, by maintaining the conditions of the surroundings as constant as possible, and by making the observations according to a well-standardized routine. The irregularities in a series of weighings may be due, for instance, to slight changes in the thermal insulation, in lighting, or in the time consumed in the manipulation. Consequently, these may be obviated by placing the source of light perfectly symmetrically with respect to the two halves of the beam, and by enclosing the balance in a good conducting metallic case. Likewise, when using manometers or precision thermometers, it is necessary to read the mercury column always either when it is rising or falling, otherwise the varying adhesion of the mercury to the glass of the capillary may introduce significant fortuitous errors.

---

[1] Smith and Wojciechowski, Rocznicki Chem., *16*, 194 (1936).

(b) *The personal equation of the observer.* The same instrument in the hands of several workers may exhibit remarkable differences in sensitivity, even though the workers are equally careful. This is due obviously to differences in the acuteness of one or the other of their senses, and the same observer may exhibit similar irregularities if his physiological condition (health or fatigue) changes noticeably. The enormous differences in the sensitivity of the eye after it has been rested in the dark or been fatigued by the light is well known, especially when judging slight differences in shades and intensities.

These conditions can be remedied by grouping the findings of several observers, or by increasing the possible accuracy of the measurements by fitting the equipment with auxiliary instruments, such as verniers.

(c) *Multiplication of observations.* The precision of results can be increased by one decimal place by taking the mean of a number of readings, but it must never be forgotten that this operation has no influence on the absolute accuracy of the result. The elimination of fortuitous errors in no way affects any systematic errors which may be present.

For instance, only an illusory precision is attained in the determination of viscosities by replacing a seconds counter with a recording chronograph when measuring the time of outflow, unless there is previous assurance that the capillary used conforms to the theoretical conditions of the outflow of liquids demanded by Poisseuille's law.

Direct and indirect measurements. Either of these methods, depending on conditions, can be selected in order to increase the precision and the sensitivity of measurements.

(a) *Direct measurements.* In a great many cases where a high degree of precision is desirable, an effort is made, for physiological reasons, to reduce the readings to measurements of length. It is easy to distinguish, to within about one tenth, the interval between two divisions on a scale, if they are marked with adequate delicacy. In this way, the sensitivity of the measurement is raised by one decimal. Thus, the use of a balance is really reduced to the reading of the position of a pointer on an index; that of an electrical resistance to the determination of the position of a movable slide along a metallic wire; the reading of a temperature to the rise of the level of a column of liquid in front of a scale, etc.

(b) *Indirect measurements.* These are the more common. The constant to be measured results from a calculation that involves different elements. The error in the final result obviously will depend on the magnitude of the errors in the evaluation of each of these factors.

The fundamental principle that should serve as a guide in adjusting indirect measurements is the balancing of factors. Each of these must be known to within a suitable degree of accuracy. It will be useless and often even harmful, because of all sorts of complications that arise, to exaggerate the precision of one of these factors without troubling to do the same for the others. In fact, the final precision depends to almost the same degree on the precision of each of the measurements contributing to the result, if these are well balanced. However, if one of the factors is notably of lower accuracy than all the rest, the precision of the whole will depend on this one alone.

Disregard of this fundamental consideration has led many authors to self-deception about the accuracy of their measurements. Collardeau [1] showed that the coefficients of expansion of mercury expressed to ten decimals, as given by Regnault as the result of his classic studies, are actually known only to the fourth place. The error committed by such a man ought to give pause to all experimenters with respect to the necessity of being prudent and modest in this regard.

There is only one case where there is advantage in considerably increasing the accuracy in the determination of certain factors. This arises when it is possible, without wantonly complicating the experimental method, to reduce enormously the error of all the factors save one, in such a way that the final precision will coincide with that of the least accurate factor.

Example: The determination of a dipole-moment is essentially affected by the error in the measurement of the dielectric constant, while the error in the concentration measurement is practically negligible.

The influence of impurities on the samples studied is too seldom taken into account in such considerations, and hence is reëmphasized here. The numerical evaluation of this source of error is difficult, but nevertheless it exerts a tremendous, almost preponderant, influence on the magnitude of the systematic error.

---

[1] Collardeau, *Les Approximation dans les mesures physiques.* Paris, 1906.

CHAPTER XX

THE BEST POSSIBLE USE OF EXPERIMENTAL DATA

THE various types of errors that must be distinguished are:

(a) *Absolute and relative error.* The absolute error is the difference between the observed value and the exact value of the constant being determined, while the relative error is the ratio of the absolute error to the quantity that is being determined. It is quite evident that it is the relative error which is of significance in the great majority of cases.

(b) *Maximum error, minimum error, mean error.* If a measurement is repeated several times, and if the exact result to be obtained is known, it is possible to distinguish immediately which of all the experimental measurements shows the maximum error (taking no account of the sign) and which the minimum error. The mean error (e_m) is the arithmetical mean of the errors (r) of all the observations, n in number, added without regard to their algebraic sign:

$$e_m = \frac{\Sigma r}{n}.$$

How can the most probable value of the quantity being measured be derived from diverse measurements of the same constant, with only fortuitous errors involved?

The simplest case is presented when diverse observations are obtained from repetitions of the same experiment conducted under identical conditions. If the number of observations is increased, the answer to the foregoing question can be got by using the computations of probabilities, and the application of this method becomes more rigorous as the number of observations is increased. The following discussion will be limited to an examination of some instances in which the application of this type of calculation is particularly simple.

Distribution of fortuitous errors. If the measurement of a particular length, to within one thousandth, is repeated one hundred times, a certain number of the readings will give a mean value that can be represented by 1000. A smaller number of observations will give the value 999, and experience shows that an exactly equal number will give 1001. The readings 998 and 1002, also equal in number, will be much fewer and so on.

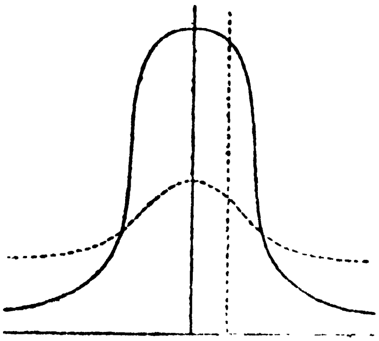


FIG. 14. The distribution of accidental errors. (Gauss' curve).

This set of observations may be represented by a diagram on which the different observed values are represented by the abscissae, and the frequency with which each has been obtained by the ordinates. If all these points are connected by a continuous line the curve shown in Fig. 14

results. The maximum ordinate corresponds to the mean value; it is most frequently observed and is the most probable value. The sharpness of this maximum will be a function of the precision of the observations since, in this case, the majority of the readings will differ but slightly from the value 1000. If the method of measurement is unreliable, the number of grossly erroneous observations will be relatively high, to the detriment of the mean value. The effect of a systematic error will be simply to displace laterally the position of the maximum by a quantity equal to the magnitude of the systematic error, but the shape of the curve is otherwise unaltered.[1]

Gauss has shown that this curve may be represented by the following equation (the error equation) which expresses the law of distribution of fortuitous errors (r):

$$y = ce^{-h^2r^2},$$

in which y is the probability of a certain error r; e is the base of natural logarithms; c and h are constants. The factors r and h are squared because the errors curve is symmetrical with respect to the y axis. c is the ordinate of the maximum value, because then the error is equal to zero and $y = c$. h indicates the position of the two points of inflexion of the curve, to the right and left of the maximum. If r has a very large or a very small value, y will tend to become zero, but will never reach this value.

The most probable value of a quantity measured a great many times. It can be shown easily that this value ought to be the algebraic mean of all the results. Let:

m = most probable value;

$s_1, s_2, s_3, \ldots$ = values observed,

---

[1] For a comparison of the curve of errors with the result of systematic experiments see Jeffreys, Phil. Trans. A, *237*, 231 (1938).

$r_1, r_2, r_3, \ldots$ = the residuals or differences between each of the observed values and the most probable value.

The following relations will hold:

$$r_1 = s_1 - m$$
$$r_2 = s_2 - m$$
$$r_3 = s_3 - m, \text{ and so on.}$$

Adding these equations, term by term:

$$\Sigma^n r = \Sigma^n s - nm.$$

According to the curve of fortuitous errors, which is perfectly symmetrical with respect to the most probable value, the deviations, positive and negative, corresponding to the residuals are exactly equal in number and magnitude. Their algebraic sum is consequently zero. If

$$\Sigma^n r = 0,\ \Sigma^n s = nm, \text{ and } m = \frac{\Sigma^n s}{n}.$$

Consequently m, the most probable value, is the algebraic mean of all the observed values.

Probable error. The most probable error (e_p) by definition ought to be such that the probability of obtaining, in each of the measurements of a series of observations, a real error numerically greater than the probable error ought to be equal to the inverse probability. It can be shown that the probable error is equal to 0.85 of the mean error (e_m):

$$e_p = 0.85\, e_m = 0.85 \frac{\Sigma^n r}{n}.$$

The importance of the probable error is that it permits the evaluation of the weights of different series of observations. These are inversely proportional to the square of the probable error of each series.

Weighting of observations. The relative value or weight of repeated observations depends on the varying conditions under which the measurements have been made. In the course of a series of measurements certain conditions of the experimental environment are not always exactly the same. The observer gradually grows tired and a host of other imponderables, whose importance it is difficult to estimate, generally makes one series of measurements more concordant than another. The weights of these diverse series of measurements can be determined only as a function of their mean error and of their probable error.

If the observations have different weights, each of the well-made ones is equivalent, to some extent, to the mean of several less concordant observations. In calculating the final value, it will be necessary therefore to include this factor, by taking the mean of the individual values only after each of them has been multiplied by the weight assigned to it. The observations with great weight are obviously those made most carefully.

For example, two series of determinations have been made on the density of a gas prepared by two different chemical methods. The experiments showed that one of these series had a probable error double that of the second. The weight of the second series is therefore four times that of the first, and each of the observations of the good series is worth four of the other. Under such conditions, it is obviously of great importance that the worker thoroughly analyze his methods of measurement before putting them to use.

The weighting of observations is involved in the calculation of the most probable value, and conversely the latter serves as the point of departure in calculating the weights of different observations. The most probable value of the constant studied can be definitely fixed only by a gradual process of successive approximations.

CHAPTER XXI

THE THEORY OF LEAST SQUARES[1]

THE choice of the most probable value of a physical quantity, that has been the subject of numerous experimental determinations, may be made in all cases, either simple or complex, by applying the theory of least squares. Only the fortuitous errors are taken into account, no consideration being given to the systematic errors to which the computation of probabilities is not applicable.

Fundamental statement. The most probable value of a quantity measured a large number of times is the one in which the sum of the squares of the errors is a minimum.

Proof: Given n observations,

$$s_1, s_2, s_3 \cdots s_n,$$

of a constant whose most probable value is m, from which each of the observed values differs respectively by the error:

$$r_1, r_2, r_3 \cdots r_n,$$

so that:

$$\left.\begin{array}{l} s_1 = m - r_1 \\ s_2 = m - r_2 \\ s_3 = m - r_3 \\ \cdot \\ \cdot \\ \cdot \\ s_n = m - r_n \end{array}\right\} \text{(a).}$$

---

[1] This very elementary discussion is based on Weld, *Theory of Errors and Least Squares.* New York, 1916.

The errors $r_1, r_2, r_3 \cdots r_n$ are distributed according to the curve of fortuitous errors; hence the probabilities:

$$y_1, y_2, y_3 \cdots y_n$$

of these errors can be calculated by the error equation of Gauss:

$$\left.\begin{array}{l} y_1 = ce^{-h^2r_1^2} \\ y_2 = ce^{-h^2r_2^2} \\ y_3 = ce^{-h^2r_3^2} \\ \cdot \\ \cdot \\ \cdot \\ y_n = ce^{-h^2r_n^2} \end{array}\right\} \text{(b).}$$

This gives a group of simultaneous equations, which ought to be satisfied at the same time since all the values of r: $r_1, r_2, r_3 \cdots r_n$, have been observed under the same conditions.

On the other hand, the total probability Y that all the equations (b) will be satisfied simultaneously is by definition equal to the product of the partial probabilities: $y_1, y_2, y_3 \cdots y_n$; or:

$$Y = y_1y_2y_3 \cdots y_n = c^ne^{-h^2(r_1^2+r_2^2+r_3^2 \cdots +r_n^2)}.$$

If m, and consequently $r_1, r_2, r_3 \cdots r_n$, are so chosen as to have the most probable value, Y ought to be as great as possible and consequently the exponent $(r_1^2 + r_2^2 + r_3^2 \cdots + r_n^2)$ should be as small as possible. However, $r_1, r_2, r_3 \cdots r_n$ are the errors, of which the sum of the squares should be a minimum if m, which has served to determine $r_1, r_2, r_3 \cdots r_n$, has the most probable value. This is the principle of least squares.

This principle will now be applied to the examination of n observations, having the same weight, made on the same quantity. It follows that $r_1^2 + r_2^2 + r_3^2 + r_n^2 = \Sigma^n r^2$ should be the minimum, and consequently also, from equations (a):

$$\Sigma^n r^2 = (s_1 - m)^2 + (s_2 - m)^2 + (s_3 - m)^2 \cdots + (s_n - m).^2$$

Differentiating this equation with respect to m gives:

$$\frac{d}{d_m}\Sigma^n r^2 = -2[(s_1 - m) + (s_2 - m) + (s_3 - m) \cdots + (s_n - m)] = 0.$$

Assuming that:

$$nm = s_1 + s_2 + s_3 \cdots s_n \quad \text{(c)}$$

it follows that $\Sigma^n r^2$ will become zero and Y infinite.

The most probable value of m corresponding to the greatest possible value of Y is that which satisfies equation (c), hence:

$$m = \frac{s_1 + s_2 + s_3 \cdots s_n}{n},$$

or stated otherwise, the most probable value of m is the algebraic mean of all the observed values. This is a well-known fact that was discussed in the preceding chapter.

Application: the study of a series of measurements of a quantity which is a function of a single independent variable, and where the number of observations exceeds the number of unknowns.

This problem arises frequently, as in the determination of the most probable coefficient of expansion of a material for which there are available a large number of measurements of the specific volume at different temperatures.

Demonstration: Given n observations, carrying l unknowns, n being greater than l; to find the most probable values of l.

Use of the normal equations. The preceding n observations give rise to an equal number of equations of the first degree:

$$s_1, s_2, s_3, \cdots s_n,$$

containing, in all, l unknowns:

$$q_1, q_2, q_3, \cdots q_l.$$

In this system of simultaneous equations of the first degree, the most probable values to be calculated for the l unknowns will be:

$$m_1, m_2, m_3, \cdots m_l.$$

The experimental data provide directly the system of n simultaneous equations (*observation equations*):

$$\begin{aligned} s_1 &= a_1q_1 + b_1q_2 + \cdots + k_1q_l \\ s_2 &= a_2q_1 + b_2q_2 + \cdots + k_2q_l \\ &\cdot \\ &\cdot \\ &\cdot \\ s_n &= a_nq_1 + b_nq_2 + \cdots + k_nq_l, \end{aligned}$$

to which correspond an equal number of *equations of residuals:*

$$\begin{aligned} r_1 &= s_1 - (a_1m_1 + b_1m_2 + \cdots + k_1m_l) \\ r_2 &= s_2 - (a_2m_1 + b_2m_2 + \cdots + k_2m_l) \\ &\cdot \\ &\cdot \\ &\cdot \\ r_n &= s_n - (a_nm_1 + b_nm_2 + \cdots + k_nm_l), \end{aligned}$$

which also may be written, by letting $B_1 = s_1 - (b_1m_2 + \cdots + k_1m_l)$, etc.:

$$\begin{aligned} r_1 &= -a_1m_1 + B_1 \\ r_2 &= -a_2m_1 + B_2 \\ &\cdot \\ &\cdot \\ &\cdot \\ r_n &= -a_nm_1 + B_n\,, \end{aligned}$$

which give then:

$$\Sigma^n r^2 = (-a_1m_1 + B_1)^2 + (-a_2m_1 + B_2)^2 \cdots + (-a_nm_1 + B_n)^2.$$

However by the theory of least squares, $\Sigma^n r^2$ should be a minimum; its partial derivative ought then to be zero. Differentiating first with respect to m_1:

$$\frac{d}{d_{m_1}}\Sigma^n r^2 = -2a_1(-a_1m_1 + B_1) - 2a_2(-a_2m_1 + B_2) - \cdots -2a_n(-a_nm_1 + B_n) = 0 \text{ (d)}.$$

Finally, dividing by 2, and replacing the B's by their values:

$$\begin{aligned} &-a_1(-a_1m_1 + s_1 - b_1m_2 \cdots -k_1m_l) \\ &-a_2(-a_2m_1 + s_2 - b_2m_2 \cdots -k_2m_l) \cdots \\ &-a_n(-a_nm_1 + s_n - b_nm_2 \cdots -k_nm_l) = 0. \end{aligned}$$

This is the *normal equation of the system* in m_1; l of these can be set up, i.e. as many as there are unknowns. In this way, the n observations all contribute to form the l simultaneous equations containing l unknowns, so there is no longer any indetermination.

For instance, a platinum wire, one meter in length and forming part of a Wheatstone bridge, has been calibrated by measuring successively the resistance of the first ten centimeters, then of the first twenty, the first thirty, and so on. Assuming that the wire is perfectly uniform, what is the total resistance of the wire (x), and what is the resistance of the connections (c), which must be eliminated? In the following table the resistances (in ohms) are given as a function of the length studied:

centimeters	10	20	30	40	50	60	70	80	90	100
resistance	0.116	205	295	388	503	595	675	760	850	926

To these ten experiments there correspond ten observation equations:

$$\begin{aligned} 0.1x + c &= 0.116 \\ 0.2x + c &= 0.205 \\ &\cdot \\ &\cdot \\ &\cdot \\ x + c &= 0.926. \end{aligned}$$

There are then ten observation equations and only two unknowns. It is necessary, first of all, to form the two normal equations of the first degree corresponding to these unknowns. The following rule facilitates this task:

In order to form normal equations in the case of first degree observation equations, it is necessary to calculate the value of the residual, r, of each observation, to multiply this by the coefficient of the first unknown, to add the products obtained, and equate the sum to zero. This gives the first normal equation. This same method is employed to produce as many normal equations as there are unknowns. Nothing remains then but to solve the resulting system of simultaneous equations.

In the present case the equations of residuals are:

$$\begin{aligned} r_{10} &= 0.116 - (0.1x + c) \\ r_{20} &= 0.205 - (0.2x + c) \\ &\cdot \\ &\cdot \\ &\cdot \\ r_{100} &= 0.926 - (x + c). \end{aligned}$$

The two normal equations are:

$$0.1(0.116 - 0.1x - c) + 0.2(0.205 - 0.2x - c) + \cdots + (0.926 - x - c) = 0 \quad (1)$$

$$(0.116 - 0.1x - c) + (0.205 - 0.2x - c) + \cdots + (0.926 - x - c) = 0 \quad (2)$$

These, on reduction, give:

$$3.85x + 5.5c = 3.686 \quad (1)$$

$$5.5x + 10c = 5.313 \quad (2)$$

from which: $x = 0.926$ ohms and $c = 0.022$ ohms.

CHAPTER XXII

UTILIZATION OF THE OBSERVED VALUES OF A QUANTITY WHEN THE NUMBER OF OBSERVATIONS EXCEEDS THE NUMBER OF UNKNOWNS

THIS problem has just been treated algebraically with the aid of the method of least squares. However, in the great majority of cases the number of usable observations is not sufficient nor are they precise enough to justify the long and tedious calculations required in the application of this theory. Furthermore, this operation also requires a previous knowledge of the algebraic function connecting the experimental results with each other, a condition that is rarely fulfilled in practice. Consequently, the objective must ordinarily be reached by methods that are less trustworthy but more rapid. A discussion of these follows.

(a) *Algebraic solutions.* If the phenomenon being studied has been the subject of a profound theoretical examination, and if the form of the law under consideration is therefore known beforehand, the role of the observer is simplified. His task is to find the exact value of the stoichiometric coefficients anticipated by the formula and characteristic of the substance, and then to verify if the individual determinations do not diverge too much from the values calculated from the formula being tested. For instance, if a reaction constant is to be calculated, ordinarily it is thought sufficient to combine the results two by two with the aid of known theoretical formulae and to demonstrate that the constant does not oscillate between too wide limits. Sometimes when the constancy is postulated *a priori*, the experimental findings are used simply to decide between the various possible theoretical formulae that correspond to different mechanisms of the reaction.

If no theoretical formulae have been set up or if they prove inadequate, the observations must be related to each other by means of a purely empirical formula, whose most suitable form has to be sought by trial. Starting from a knowledge of the variables that must be taken into consideration, more and more complex types of formulae are tried successively. By calculating each time the constants of this formula, beginning with selected observations, it can be determined if the agreement of the formula with the results of other experiments is adequate.

Examples of the most common types of formulae are:

(1) Development in series:

$$x = a \pm bt \pm ct^2 \pm dt^3 \pm \cdots$$

$$x = a \pm \frac{b}{t} \pm \frac{c}{t^2} \pm \frac{d}{t^3} \pm \cdots \quad ;$$

(2) Logarithmic equations:

$$\log x = a \pm b \times \log t \quad ;$$

(3) Hyberbolic equations:

$$xy = \text{const.}$$

In the absence of any guide, the task may often be simplified by not seeking directly the formula that represents precisely the phenomenon in question. Rather, an attempt is made to use a simple empirical formula and to see how the differences between the observed and the calculated values behave with respect to this trial formula. In this way, a fair idea can be gained of the type of corrections to be applied to the first formula to bring it into closer accord with the facts. If an equation of the first degree is found to be inadequate, the addition, for example, of a term of the second degree will show whether the goal is being approached.

A typical example of the interesting results that may be obtained by this method, where the difficulties to be overcome are considered one after the other, is given by Callendar's formula, which represents the resistance of platinum wires as a function of the temperature. Above 0° the resistance increases almost linearly in accord with the formula:

$$R^T = R^\circ + kT.$$

For low temperatures, on the contrary, this expression yields values for R that are less than those observed or, conversely, T calculated from the formula is too low. Travers[1] showed that excellent results are obtained by substituting $(t + D)$ for T in the original formula, if

$$D = \frac{1.5t}{100} \times \left(\frac{t}{100} - 1\right).$$

When this empirical method must be used to discover the formula best suited to represent the numerical results, it is essential always to take carefully into account certain limiting conditions with which the formula ought necessarily comply. For example, the freezing curve of a mixture ought to begin at the melting point of one of the components. Pierre[1] would have been able to correct certain of his empirical formulae for the expansion of liquids if he had noted that they led to the prediction of the existence of a maximum density (like that possessed by water) in a region of temperatures easily accessible to experimentation. These tests would have demonstrated to him immediately that his formula could not hold rigorously for chloroform, for example. Such mistakes ought to make workers very suspicious of every conclusion that is based on the mere extrapolation of an empirical formula.

---

[1] Travers and Gwyer, Z. physik. Chem., *52*, 446 (1905); Proc. Roy. Soc., (London), *74*, 528 (1905).

(b) *Graphic methods.* Here again, efforts should be made to use diagrams that contain only simple forms such as straight lines, arcs of circles, equilateral hyperbolae, etc.

To construct a diagram rationally, it is necessary to choose the scale, the respective proportions of the two coordinate axes, and the width of the line connecting the points, so that the anomalies of the experimental data may be distinctly shown, without however exceeding the degree of precision of the observed values. Thus if the experiments when plotted produce a graph that approximates a straight line, the axes of the coordinates should be so placed that the curve appears approximately as a diagonal. In this way, the irregularities of the abscissae are made just as apparent as those of the ordinates. To do otherwise involves the risk of masking certain abnormalities, and is advisable only if this very result is desired because of a rather great inequality in the precision of measuring the two variables involved (Fig. 15).

For the same reason, the thickness of line of the experimental curve ought not to exceed the distance that corresponds to the minimum error on the diagram. The intuitive feeling that the continuity of the phenomenon ought to give rise to a curve without abrupt inflections should be a guide in constructing the diagram. Such smooth curves can be drawn with the aid of a French curve, or of flexible tape which easily takes on the sinuosities of experimental curves, if the latter are not too capricious. The regular distribution of the tension applied to such elastic tape is especially well accomplished if slender wooden strips or glass rods are used for this purpose. These break if their limit of elasticity is exceeded, and do not yield subtly as do steel bands, which then retain a more or less marked point of inflection.

---

[1] Pierre, Ann. chim. phys., [3] *33*, 199 (1851).

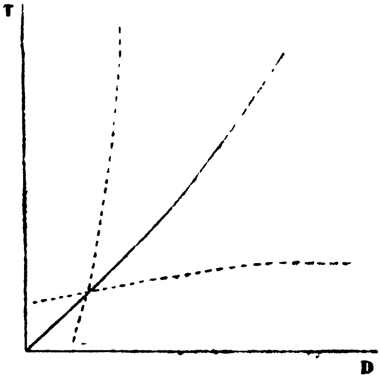


FIG. 15. Diagram showing the variation of a constant (such as D) with temperature.

Aided by the foregoing recommendations a tentative curve is drawn, keeping in mind the feeling of the continuity of the phenomenon, when its variables change progressively. The curve should reflect the continuity. Another guide is the necessity of making the curve pass not exactly through all the experimental points, but through a mean position such that none of these points is off the curve by a distance greater than the probable error.

In certain cases, there are mathematical rules that facilitate the drawing of these curves, since they fix absolutely one or several points of the curve whose general course is to be plotted. The curve ought either pass through the origin of the system of the chosen coordinates or, if it is a straight line, it must pass through a point whose ordinate equals the mean of the ordinates of all the observations and whose abscissa equals the mean of all the abscissae.[1]

It is often advantageous not to draw a diagram directly with respect to the variables of the observations, but first to change these in a suitable manner. For instance, if the curve to be drawn is an hyperbola, it is preferable to plot the straight line that corresponds to its reciprocal. In the case of ideal solutions, it is easier to plot the straight line of the isothermal vapor tensions at all concentrations than the corresponding curve of the isobaric boiling points.

If the extrapolation of a graph leads to infinity it is preferable to plot the reciprocals of the abscissae so that their zero values will be approached on extrapolation. For instance, the study of the limiting conductivities at infinite dilution should be replaced by that of the limiting conductance at zero concentration.

An exponential curve should be replaced by its logarithmic form, because in this case all the curves obtained may be superimposed by simple translation. An example is Raveau's study [2] of corresponding states.

It is better to use diagrams that permit an indirect verification of the experimental findings. An instance is the rule of Ramsay and Young [3] by which errors in the measurements of the saturated vapor pressure of pure liquids can be detected by comparing them with the values shown by a well-studied substance, such as water or mercury.

---

[1] Roeser, Phys. Rev., [2] *9*, 80 (1917).

[2] Raveau, J. Phys., [3] *6*, 432 (1897).

[3] Ramsay and Young, Phil. Mag., [5] *20*, 515 (1885); *21*, 33; *22*, 37 (1886).

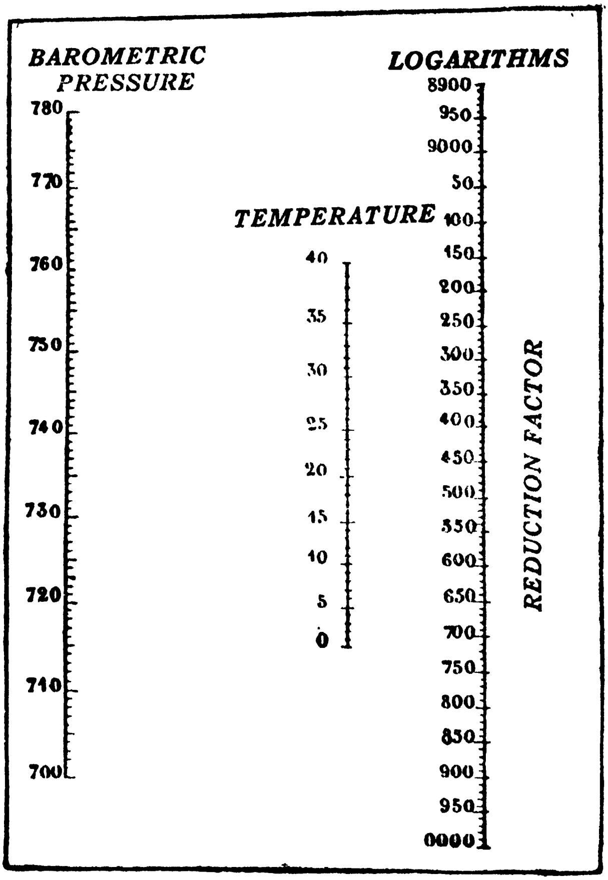


Fig. 16. Nomograph for the reduction to standard conditions (0° C. and 760 mm.) and to the condition of a water-free gas of the volume of one cc. of air saturated with water vapor, and measured at different temperatures and pressures.

If more than two variables are to be considered, it is logical to use solid diagrams of three (or n) dimensions, but the models which result do not lend themselves very well to quantitative use. Consequently, it is preferable to obviate the difficulty by employing plane diagrams. This may be accomplished:

(1) The number of variables is reduced by setting up supplementary conditions. For example, in problems involving the phase rule, the vaporization equilibria of a ternary system may be represented on a plane triangular diagram, provided that only isobaric or isothermal systems are considered.

(2) Other types of representation, such as graphic tables or nomographs, may be used. For instance, the correction term for reducing the reading of the volume of a gas saturated with moisture to that which it would be if the gas was perfectly dry and under normal conditions of temperature and pressure, is found easily by this method (Fig. 16).

PART IV

THE WAY TO FIND IN THE LITERATURE THE BEST METHOD OF PURIFICATION AND THE MOST PROBABLE VALUE OF THE CONSTANTS OF PURE MATERIALS. EXAMPLES AND APPLICATIONS

CHAPTER XXIII

SPECIALIZED LABORATORIES AND STUDIES

The exact determination of physical constants is one of the principal aims of stoichiometry. In what laboratories are such studies made; where are they published? This chapter also deals with the method of finding in the abundant literature all the apposite numerical data, and how to make a choice from them.

Specialized laboratories. When physico-chemical studies were begun, the determination of constants was the object of the labors of many isolated workers, but as the number of substances to be studied increased and as the accuracy required became, at the same time, higher this type of research was concentrated more and more in the hands of specialists. At the present time, the most important work in this field is done in institutes, usually supported by the government, and provided with ample equipment placed at the disposal of a staff of skilled technicians. All these laboratories were founded for the purpose of improving the methods used in industry, to develop military resources, etc. However, they have been forced to deal more and more with such problems of pure science as require for their solutions a collaboration of efforts beyond that which may be expected of an individual scientist limited to his own resources.

The French chemist and physicist, Henri Regnault (1812–78) deserves the credit for initiating this modern movement. His work, admirable for its time, is still, in many cases, the firm foundation of the progress of thermodynamics and of present day chemistry and physics.

(a) *France.* The first collective project, born of the imperative needs of unifying the systems of weights and measures used in the civilized countries, was the foundation of the Bureau International des Poids et Mesures, at Sèvres. The principal aim of its work has been the construction and profound study of the fundamental standards of the metric system. Later, there developed in this laboratory a series of very important researches on thermometric measurements, which led to the creation of an International Advisory Commission. The researches of Guillaume on nickel steels, of prime importance to precise chronometry, were another noteworthy contribution of this laboratory.

This Bureau is an international undertaking, subsidized by a large number of governments. Its principal publications appear in the "Travaux et Memoires du Bureau International des Poids et Mesures." The decisions of the Bureau are reproduced in the Procès-Verbaux of its conferences.

Among other institutions of the same type are the Bureau de Longitudes at Paris, which publishes a year book, and the Laboratoire Central d'Electricité. These, however, play only a minor role as regards original investigation.

(b) *Germany.* The most complete type of bureau of standards is the Physikalisch-technische Reichsanstalt at Charlottenburg-Berlin. This institution was founded under the inspiration of Helmholtz. Divided into numerous sections its activities cover a wide range. Its fundamental purpose is to place the resources of pure science at the disposal of German industry, particularly when the necessary researches exceed the bounds and the means of the laboratories of a given industry. Besides very important physical studies of the equation of state of gases, of resistance thermometers, etc., the Reichsanstalt has made important contributions to the physico-chemical investigation of pure metals, of metallic salts, etc. Its "Wissenschaftliche Abhandlungen" appear irregularly. It is only necessary to leaf through the "Wärmetabellen," published in 1919 by L. Holborn, K. Scheel and F. Henning, to appreciate the variety of constants studied and to gain an idea of the enormous effort that has been made to render Germany absolutely independent of all foreign collaboration in this field.

The "Wissenschaftliche Abhandlungen" of the Normal-Eichungs-Kommission at Berlin, whose tables of the density of aqueous solutions of alcohol, sulfuric acid, etc., are classics, must be mentioned here.

(c) *United States of America.* Following the example set by the Reichsanstalt at Charlottenburg, the Bureau of Standards at Washington, with the cooperation of other American government laboratories such as the Bureau of Mines, has extended its very considerable activities over all the fields explored by its German counterpart. Among its achievements are: the work on the thermometric scale of high temperatures, studied with remarkable success by such men as Burgess, Day and Sosman; the study of the international calorimetric standard (benzoic acid); the preparation, under the direction of Washburn, of a great number of paraffins and polymethylenes in the pure state. It also sells directly to the public standard samples that have been checked by the Bureau. Besides numerous contributions to the American scientific journals, the Bureau publishes its "Journal of Research," a continuation and consolidation, since 1928, of its "Scientific Papers" and "Technological Papers," and also puts out "Annual Reports" and "Circulars."

(d) *England.* Since the Great War (1914–18), the National Physical Laboratory, at Teddington, has developed greatly under the supervision of the Royal Society of London. Among its studies, special mention should be made of the construction of the first electrical standards and, more recently, the remarkable metallographic researches of Rosenhain. The principal publication of this institute is "Reports of the National Physical Laboratory."

The National Chemical Laboratory was established about ten years ago.

(e) *Russia.* It was at the Bureau of Weights and Measures at St. Petersburg, under the direction of the Academy of Sciences, that Mendeleeff did his classic work on anhydrous ethyl alcohol. Since 1922, there has been at Moscow a government institute for the study of pure reagents. A number of interesting researches on organic standards and on inorganic reagents have been carried out there.

(f) *Holland.* In addition to the government institutions, there is the Cryogenic Laboratory of the University of Leiden. This was founded by Kamerlingh-Onnes and occupies a place in the first rank of laboratories specializing in the study of low temperatures. Its "Communications from the Physical Laboratory of the University of Leiden" now comprise almost 300 issues, and contain an invaluable fund of information.

(g) *Belgium.* The Bureau of Physical Chemical Standards was established at the University of Brussels in 1920, under the auspices of the International Union of Pure and Applied Chemistry. It strives to be a center for the preparation of pure materials and the study of their constants. Its resources are quite limited, and so it has concentrated the efforts of its laboratory and its documentary services on the study of the physical constants of organic compounds. The results of its labors have been published in the Journal de Chimie Physique and in the Bulletin de la Société Chimique de Belgique.

The better data obtained in its laboratory and those taken from a critical review of the literature have been collected in *Etalons physico-chimiques organiques*, published at Leipzig in 1939.

COLLECTIONS OF PHYSICAL CONSTANTS

Most books on chemistry contain many numerical data concerning the properties of the most varied substances. However, great difficulties are encountered as soon as information is sought about really well-established values because the original data generally are buried in a host of scattered publications, and because little critical sense is used in selecting the figures that are included in general texts.

(a) *Chemical encyclopediae.* The general treatises are usually rather unsatisfactory in this regard. An extensive documentation is given in Beilstein's *Handbuch der organischen Chemie* and its supplements, and also in Abderhalden's *Handbuch der Biochemie.* In the inorganic field, the new edition of Gmelin-Kraut, prepared under the auspices of the German Chemical Society, is a model of critical evaluation.

(b) *Collections of constants.* The need of a critical review of the data of the literature of the special field treated in this book has given rise to a number of collections of constants. The value of these will be briefly characterized.

In 1881, Rammelsberg published the first book of this kind: his *Handbuch der krystallographisch-physikalischen Chemie.* This work, remarkable for its time but now out-moded, has the peculiarity that all sorts of constants relating to the same substance were grouped together. Since then, all the tables of this type have put the values of each constant for all substances into distinct divisions.

The *Constants of Nature,* published under the leadership of F. W. Clarke, by the Smithsonian Institution at Washington, deserves mention. The first edition contained only data on the densities, boiling and freezing points of materials, but the subsequent issues were much more extensive. However, the bibliographic references are scanty.

An analogous method was followed in the compilation of the *Recueil des Constants,* published before the Great War by the Société française de Physique, under the direction of Abraham and Sacerdote. The different parts of the work are signed by their respective authors, who have assumed the responsibility for the critical choice of the values but without feeling obligated to indicate the sources from which the data were taken.

The *Physikalische Chemische Tabellen* of Landolt-Börnstein, whose fifth edition appeared in 1923, are models of their kind. The compilation was the fruit of the collaboration of numerous commissioned specialists, and the bibliographic documentation is particularly full. Supplements were published in 1927, 1929, 1931, 1939. The *International Critical Tables,* published at first under the direction of Washburn by the National Research Council of America, has a still more abundant and varied documentation. Only one numerical value, considered the most probable and selected with great care, is given for each physical quantity.

Finally, the *Tables Annuelles des Constantes et Données Numériques*, appearing since 1910, contain all the values published each year in all the fields of the physical sciences. They aspire to be as complete as possible, but give no critical review of the data.

(c) *Special compilations.* In addition to the foregoing general works, there are books that give a very complete documentation of a limited field. Notable among these are the *Recueil de Constantes Optiques*, published by Dufet under the auspices of the French Physical Society (a new edition is being prepared), and Landolt's *Das Optische Drehungsvermögen* (2nd ed. 1898), which gives data concerning rotatory power. An English translation by Long appeared in 1902. It is now obviously badly out of date. The second part of Walden's excellent work on the conductivity of solutions *Das Leitvermögen der Lösungen* (Leipzig 1924) also deserves mention.

In another field are such compilations as Seidell's *Solubilities of Organic and Inorganic Substances* (1920) which is quite complete. A voluminous supplement appeared in 1928.

The *Handbuch der physikalischen Krystallographie* by Groth is a model of its kind. Its four volumes are the fruit of a lifetime of labor.

(d) *Tables.* In order to learn the actual state of the science, not from the standpoint of a certain property but with respect to a particular material, it is necessary to consult the encyclopediae such as those cited in (a) with the aid of the tables like those of Richter and Stelzner for organic chemistry, Hoffman for inorganic chemistry and Fedoroff for the crystal kingdom.

(e) *Handbooks.* In addition to these monumental works, there are a large number of compendia or handbooks that are widely used in technical laboratories. As these are sometimes considerably behind the times, the data in them cannot always be trusted.

CHAPTER XXIV

CRITICAL APPRAISAL AND CHOICE OF PUBLISHED DATA

THE authors of most of the texts have based their choice of numerical data on a critical examination of the methods of physical measurements employed. But in general they have neglected to take sufficient account of a very important factor,—the purity of the samples studied.

To make an intelligent choice of data it is necessary, first of all, to assemble a documentation, as extensive as possible, from the original sources. There should be no hesitation in sifting the bibliographic items in a compilation published in any particular country, because these citations may give additional references to analogous works that have appeared in other countries. This part of the science is still so badly organized that it is of prime importance to check and supplement the information given by each author.

After all this material has been assembled, the most probable value of the particular constant must be selected. Quite varied considerations govern this choice.[1]

A. *The authenticity of published values.* An examination of a critical historical treatise will show that, for the most part, it consists of a survey of the degree of authenticity of the written sources, which often are available only in a form quite different from the original text. Obviously, this question seldom arises in the present connection, since the publications, whose content is being discussed here, are ordinarily accessible as printed under the direct supervision of the writer. The only point to be kept in mind is the possible inclusion of printing errors which may have slipped past the proof reader, and of errors such as omissions due to a faulty editing of the original manuscript. For instance, Richards and Mathews, in a paper on surface tension measured at 30° indicated some density values allegedly made at 20°. However, a comparison of their figures with those of other writers shows that these density measurements were very probably made at 30°, as were those of the surface tension given in the following column of their table.

---

[1] Timmermans, Helv. Chim. Act., *14*, 445 (1931):

On the other hand, the exact significance of many recorded temperatures cannot be interpreted accurately because the worker has not indicated whether or not he has applied a correction for stem exposure. Densities are often given without stating whether they refer to vacuo or to $\frac{t}{t}$ or $\frac{t}{4^\circ}$, etc.

B. *Intrinsic criteria* allow a direct appraisal of the value of a study. These criteria result particularly from a consideration of the tests of the purity of samples, as outlined in Part II of this book, if they are combined with an appreciation of the precision of the physical methods of measurement employed.

(a) If the origin of the sample or the method of purifying it do not permit the material to be obtained pure, obviously all the constants given for such a product are of debatable value. Such is the case for the saturated aliphatic hydrocarbons obtained by ordinary fractionation of mineral oils. Young,[1] and later Chavanne and Washburn,[2] succeeded in preparing pure pentane in this way, but the fractionation required months of diligent labor.

(b) If one of the constants shows that the sample is impure, all the other figures should be discarded. This holds, for instance, for compounds that do not distil at a constant temperature, or for substances whose density is clearly erroneous.

(c) A pure sample may give apparently inaccurate values for one of its constants if the calibration of the measuring equipment has been made with the aid of poor standards. For example, the thermometric scale used above 100° by Kahlbaum of Basle and his students is known to have been too low. Sometimes a correction essential to produce the desired degree of precision has been neglected.

(d) Theoretical considerations may be a useful guide in the choice of the definitive value of a constant, but it is still necessary to keep in mind all possibilities. For instance, measurements of solubility at different temperatures that give values falling on a continuous curve are obviously preferable to those that give only erratic data. However, it is still necessary to be sure that the latter are not due to the fact that the material has undergone a transformation (polymorphism, solvation, etc.). The solubilities recorded by Etard,[3] fall quite regularly on a graph, nevertheless, they inspire little confidence because he has taken no account of this last factor.

(e) Likewise, the erratic aspect of certain groups of measurements is immediately revealed with the aid of graphs. Examples are: the plotting of dispersion with the indices as a function of the reciprocal of the square of the wave length, or the construction of pressure curves of saturated vapor using the logarithms of the pressure as ordinates and the reciprocal of the absolute temperature as abscissae.

---

[1] Young, J. Chem. Soc., *71*, 446 (1897).

[2] Chavanne, Bull. soc. chim. Belg., *31*, 331 (1922); Washburn, Am. Petroleum Inst. Proc. 14th Annual Meet. Sec. III, 111 (1933).

[3] Etard, Ann. chim. phys., [7] *2*, 503 (1894).

(f) The agreement of values coming from different workers or laboratories usually testifies to their accuracy because truth alone is unique and error is multiple. However, it is necessary to be certain that these very concordant values have not all been obtained from the same samples of a material which has passed from hand to hand in the same laboratory. Sometimes allegedly new data are simply a reprinting of results previously published.

(g) The personality of the worker also plays a part. Has he made a critical study of the method of purifying his samples? Has he not exaggerated the accuracy of his measurements? Modesty on this point is too seldom a failing.

(h) Measurements by a specialist, who has made a name for himself in the field, patently carry much more weight than those of a beginner, or of one of those observers who has acquired the sad reputation of burdening the journals with hasty publications. Likewise, systematic, directed studies on a given constant are preferable to values obtained incidentally in the course of researches having a different objective. The papers of Walden contain many freezing points of organic compounds that melt below 0° C., but despite the high regard in which this scientist is rightly held, these values have no guarantee of validity because he has manifestly used an inaccurate thermometer.

(i) Finally, other considerations being equal, the most recent work is probably the better. Data obtained before 1900 are rarely still of interest, unless they were the findings of leading scientists, such as Perkin, Young, etc. However, it is necessary to be sure that the contemporary worker is quite familiar with the literature, because in the field of pure compounds the current publications contain, each year, many results which demonstrate a truly inconceivable ignorance of what has already been done.

The choice of the constants of benzene will be used to exemplify the foregoing.

Freezing point. The most careful studies are those of Richards, Carver and Schrumb. They gave, as their final result, 5.493°, a figure uncertain by 0.007° because of possible errors in the calibration of the thermometer.[1] Among the innumerable determinations of this constant by other workers, it is of interest to discuss here only those published since 1910 and above 5.50°. The value given by Young,[2] 5.58°, was obtained with an extremely pure sample, but it does not possess all the guarantees from the thermometric point of view.[3] The same is true of the later values 5.58°, published by Ewins [4] and by Gifford and Lowry;[5] and 5.51° by Kalff.[6] The value 5.60°, obtained by Meldrum,[7] referred to a product less pure than the others. The values, 5.61° given by Lorenz,[8] and 5.85° by Stratton,[9] were not determined with sufficient care to merit serious consideration.

Air is quite soluble in benzene, but produces no marked depression of the freezing point, because the cryoscopic lowering is almost exactly compensated by the elevation of the fusion temperature due to the increase of the external pressure. (See the interesting polemic on this subject between Meyer and Richards.)[1] The air can be completely expelled by a short boiling.

---

[1] Richards, Carver and Schrumb, J. Am. Chem. Soc., *41*, 2019 (1919):
[2] Young, Sci. Proc. Roy. Dublin Soc., (N. S.) *12*, 374 (1910).
[3] Richards and Shipley, J. Am. Chem. Soc., *36*, 1825 (1914).
[4] Ewins, J. Chem. Soc., *105*, 350 (1914).
[5] Gifford and Lowry, Proc. Roy. Soc. (London) (A), *104*, 434 (1923).
[6] Kalff, Thesis Amsterdam, 1924.
[7] Meldrum, Chem. News, *113*, 266 (1916).
[8] Lorenz and Posen, Z. anorg. allgem. Chem., *96*, 219 (1916);
[9] Stratton and Partington, Phil. Mag., [6] *48*, 1059 (1924).

If benzene issues from the end of a condenser in contact with moist air it becomes saturated with water. There results a cryoscopic lowering of 0.100°, according to Sidgwick [2] and Crowther [3] and of 0.93°, according to Richards, Carver and Schrumb.

CRITICAL CONSTANTS OF BENZENE

Worker	T_c	P_c
Sajotchewsky (1879)	280.6°	49.5 atmospheres
Ramsay (1881)	291.7	60.5
Schmidt (1891)	296.4	—
Altschul (1893)	290.5	50.1
Radice (1899)	288.1	—
Schamhardt (1908)	288.68	49.55
Young (1910)	288.5	47.89

The critical temperature may be chosen from these seven values, and the critical pressure from these five. The figures are too different for their mean to be taken, as van Laar [4] proposed in his discussion with Dolezalek.[5]

How is the choice to be made? The figure of Sajotchewsky [6] is very good if compared with modern values, but it is much too early to carry much weight. That given by

---

[1] Meyer, Z. physik. Chem., *90*, 721 (1915).

[2] Sidgwick, J. Chem. Soc., *117*, 1340 (1920).

[3] Crowther and Puri, Proc. Roy. Soc., (London) (A), *106*, 234 (1924).

[4] van Laar, Z. physik. Chem., *83*, 599 (1913).

[5] Dolezalek, Z. physik. Chem., *83*, 40 (1913).

[6] Sajotchewsky, Beibl. Ann. Physik *3*, 741 (1879).

Ramsay[1] has the authority of a great name, but it must be noted that he was only a beginner in this field at that time. His much too high value of the critical pressure seems to indicate the presence of a significant impurity. Finally, Schmidt[2] gives only a critical temperature, and this is quite out of line. There remain the four more recent measurements. The excellent agreement of the three latest determinations of the critical temperature leave no doubt: this temperature cannot be far from 288.5°.

As to the critical pressure, it is pertinent to call attention to the difficulty of introducing a liquid into a Cailletet tube without also bringing in a trace of dissolved air. The presence of traces of air suffice to raise the critical pressure appreciably. Consequently, it seems best to give the preference to the lowest value (47.9 atmospheres) as determined by Young.[3] The Schamhardt value[4] agrees better with those of Sojatchewsky and of Altschul,[5] but these latter do not carry great weight. Even though Schamhardt worked with all the resources of a well-equipped laboratory, that of van der Waals in Amsterdam, he was, nevertheless, a mere beginner in comparison with a recognized specialist like Young.

---

[1] Ramsay, Proc. Roy. Soc., (London), *31*, 194 (1881).
[2] Schmidt, Ann., *266*, 266 (1891).
[3] Young, Sci. Proc. Roy. Dublin Soc., (N. S.) *12*, 374 (1910).
[4] Schamhardt, Thesis, Amsterdam 1908.
[5] Altschul, Z. physik. Chem., *11*, 577 (1893).

CHAPTER XXV

EXAMPLES OF PURE MATERIALS

I. *Water*, of all materials, lends itself best to a meticulous purification. The method used universally is distillation, conducted differently according to the end in view.

(a) *Thermometry.* The distillation is carried out in glass apparatus freed of surface alkali by treatment with steam, as recommended by Ostwald. The head fractions which contain dissolved gases (air, CO_2, NH_3) are discarded, and likewise the residue which contains the non-volatile impurities is rejected. The pure water obtained thus can be used directly for thermometric purposes. If the ice formed from distilled water is broken up and the water produced by melting these fragments is allowed to drain off freely, it reproduces the zero point within approximately 1/100th of a degree.

(b) *Electrochemistry.* Water treated as just described is not pure enough. It should be re-distilled *in vacuo* in either platinum or quartz apparatus so as to obtain a fraction of minimum specific conductivity (0.38×10^{-7} at 18°, according to Kohlrausch).[1]

II. *Ethyl alcohol* is important as the base of alcoholometry. It has been the subject of a large number of studies.

---

[1] Kohlrausch and Heydweiller, Z. physik: chem., *14*, 317, (1894).

The most prominent are those of Gay Lussac,[1] Mendeleeff,[2] Crismer,[3] and Osborne.[4]

Metallic sodium and barium hydroxide are not suitable for drying alcohol, because the equilibria between the resulting alcoholates and the hydrates are in favor of the alcohol so that a small part of the water remains uncombined or unaffected. Crismer has shown that quick lime does not offer this disadvantage.

The tests of purity most usually applied to alcohol are, besides the density, the index of refraction used by Andrews,[5] and the critical solution temperature in gasoline studied by Crismer. This latter test will show the presence of 1/20,000th of water, corresponding to a change of 0.1° in the critical solution temperature. If the alcohol is fractionated so as to concentrate the water into the azeotropic mixture, the presence of 1/100,000th of water can be disclosed by this criterion.

An entirely different method of dehydrating aqueous alcohol was devised by Young.[6] The water is eliminated in the form of a ternary water-alcohol-benzene (or hexane, ethylene dichloride, etc.) mixture, whose boiling point is much lower than any of its components or their binary mixtures (p. 80). The residue of such a fractionation is anhydrous alcohol. This method is used industrially.

Results: Density $\frac{25^\circ}{4^\circ}$ *in vacuo* of dehydrated alcohol (Osborne)

---

[1] Gay Lussac, Ann. chim. phys., [2] *11*, 296 (1819).

[2] Mendeleeff, Pogg. Ann., *138*, 103, 230 (1869).

[3] Crismer, Bull. soc. chim. Belg., *18*, 18 (1904).

[4] Osborne, McKelvy and Bearce, Bull. Bur. Standards (U. S.), *9*, 327 (1913).

[5] Andrews, J. Am. Chem. Soc., *30*, 353 (1908).

[6] Young and Fortey, J. Chem. Soc., *81*, 717 (1902).

Lime: 0.785059
Aluminum amalgam: 0.785058.

Saturated with air (0.2 cc. of air per cc. of alcohol) the density increases by 0.000084.

The presence of 0.01% aldehyde raises the density 0.00002. The presence of 0.1% ether lowers the density 0.00004.

The density given by several workers:[1]

	Desiccant	*Density* $\frac{15^\circ}{4^\circ}$
Mendeleeff	CaO and BaO	0.79363
Cook	CaC_2	0.79357
Crismer	CaO	0.79366
Winkler	Ca	0.79363

Gillo [2] has shown that it is easy to prepare ethyl alcohol whose $\Delta t = 0.000^\circ$. The determination of impurities by physical and chemical methods showed that the sample contained:

less than 10^{-4} % acetaldehyde
" " 10^{-3} % methyl ethyl ketone
" " 10^{-4} % furfurol
" " 5×10^{-4} % methyl alcohol
" " 3×10^{-4} % methyl acetate
" " 10^{-4} % carbon bisulfide
" " $5 \times 10^{-4} - 10^{-3}$ % water.

III. *Oxygen.* Measurement of the weight of the normal liter to determine the atomic weight.[3]

---

[1] Mendeleeff, Pogg. Ann., *138*, 103, 230 (1869); Cook and Haines, Proc. Iowa Acad. Sci., *9*, 86 (1901); Crismer, Bull. soc. chim. Belg., *18*, 18 (1904); Winkler, Ber., *38*, 3612 (1905).

[2] Gillo, Bull. soc. chim. Belg., *48*, 341 (1939):

[3] Moles, J. chim. phys., *19*, 100 (1921).

Pure oxygen is usually obtained by heating very pure potassium chlorate or permanganate, that is, free of organic matter. This operation is carried out *in vacuo* in glass equipment. The gas passes over pellets of potassium hydroxide to remove carbon dioxide, over phosphorus pentoxide to remove water, bubbles through mercury to decompose any ozone present, through a Jena G 5 filter to remove solid particles, and is then subjected to fractional distillation.

The tests of purity employed are: constancy of the tension of the saturated vapor during the liquefaction [realizable within ±0.05 atmosphere],[1] the value of the critical constants, and especially the density at 0°.

	T_c	P_c
Wroblewski (1885)[2]	−118.0°	50.0 atmospheres
Olzewski (1883)[3]	−118.8	50.8
Onnes (1914)[4]	−118.8	49.713
Cardoso (1915)[1]	−118.0 ± 0.1	49.3 ± 0.1

Boiling point under normal pressure:

Onnes and Braak (1908)[5]	−182.995°
Siemens (1913)[6]	−182.99

Weight of a normal liter at 0°/4:

Rayleigh (1893)[7] 1.42905 ($KClO_3$)

---

[1] Cardoso, J. chim. phys., *23*, 829 (1926).

[2] Wroblewski, Wied. Ann. *25*, 402; *26*, 134, (1885); Monatsh:, *6*, 204, (1885).

[3] Olzewski, Compt. rend., *100*, 350, (1885).

[4] Onnes, Dorsman and Horst, Commun. Phys. Lab. Leiden *145 b*, (1914).

[5] Onnes and Braak, *ibid.*, *107a*, (1908) corrected by Cath, *152d*, (1918).

[6] Siemens, Ann. Physik *42*, 871, (1913).

[7] Rayleigh, Proc. Roy. Soc., *53*, 134, (1893).

Morley (1896) [1]	1.42900 (Electrolytic)
Scheuer (1913) [2]	1.42906 ($KMnO_4$)
Germann (1914) [3]	1.42905 ($KMNO_4$)
Mean	1.42908, corrected by Moles to 1.4289 (1.42894) in 1921 [4]

IV. *Standard metals:* "Normierte Metalle" of the Reichsanstalt,[5] prepared and analyzed under the supervision of this institution, and sold with its guarantee. The same is true of the materials sold by the Bureau of Standards at Washington.[6]

Purpose: Thermometric or analytical standards.

Example: Pure zinc prepared by fractional distillation of very pure metal, then re-melted and cast in graphite molds (cylindrical ingots of 10 gm.).

PURE ZINC

	Sample furnished by	
Analysis	Washington	Charlottenburg
Fe (per 250 g.)	0.005%	0.001%
Pb (" 250 g.)	0.0004%	0.021%
Cd (" 250 g.)	0.0018%	0.021%
As (" 50 g.)	trace (0.001%)	trace
Sb (" 50 g.)	0	0

---

[1] Morley, Z. physik. Chem., *20*, 68 (1896); Smithsonian Contributions to Knowledge, 1895.

[2] Scheuer, Sitzber. Akad. Wiss. Wien, *123*, IIa, 931, (1914).

[3] Germann, J. Chim. phys., *12*, 100, (1914).

[4] Moles, Les Determinations physico-chimiques des poids moleculaires et atomiques des gaz, pp. 31–32. (Collection Scientifique de l'Institut international de Corporation intellectuelle, Paris, 1938.)

[5] Mylius, Z. anorg. allgem. chem., *74*, 407 (1912); Z. Elektrochem., *23*, 152 (1917); also the Annual Reports of the Reichsanstalt, summarized in the Z. Elektrochem. since 1915.

[6] Circulars of the Bureau of Standards, *14*, 1916; *25*, 1917; *66*, 1917.

PURE ZINC—*Continued*

Analysis	*Sample furnished by* Washington	Charlottenburg
Th (per 250 g.)	0	0
S (" 10 g.)	trace	trace
Zn (by difference)	99.993%	99.957%

The commercial product contains about 1% of impurities.

Melting point:	Day and Sossmann (1910) [1]	419.4°
	Burgess and Waidner (1910) [2]	419.4
	Holborn and Henning (1911) [3]	419.4

V. *Highly purified salts of metals:* For analytical primary standard: sodium oxalate; for calibration of thermometers: hydrated sodium sulfate.

Example: $Na_2SO_4 \cdot 10H_2O$ (Richards).[4] Pure sodium bicarbonate is dissolved in dilute sulfuric acid; the anhydrous sulfate is precipitated at 100°, filtered and re-dissolved in conductivity water. The salt is still slightly acid to methyl orange, and its transformation point is 32.54°. After two re-crystallizations it is neutral, and transforms at 32.582°; after four re-crystallizations, at 32.583 ± 0.001°. The pure commercial salt melts 0.06° too low.

VI. *Pure organic solids:* Commercial benzoic acid gives excellent specimens of this material, containing as impurities only traces of moisture retained mechanically within the crystals. This water can be removed by exposing the finely powdered material to P_2O_5 in an evacuated desiccator. Such material boils at 250.0° and melts at 122.45°. It is distributed as a thermochemical standard, with a value of 6318.0 calories per gram of acid, weighed in a vacuum and burned at 20°.[1]

---

[1] Day and Sossman, Am. J. Sci., *29*, 93 (1910).

[2] Burgess and Waidner, Bull. Bur. of Stand., *6*, 149, (1910); *7*, 3, (1910).

[3] Holborn and Henning, Ann. Physik, 4, *35*, 761 (1911).

[4] Richards & Wells, Proc. Am. Acad., *38*, 481 (1902); Z. physik. Chem., *43*, 465 (1903).

---

[1] Roth and Lamprecht, Rocznicki chem., *18*, 747 (1938).

CHAPTER XXVI

SCIENTIFIC AND TECHNICAL APPLICATION OF PURE MATERIALS

CHEMISTS have devoted considerable time and effort to define exactly the concept of chemical species, to prepare with the greatest possible care pure materials conforming to the conditions demanded by the theory, and to determine the value of their constants as exactly as possible. However, these efforts sometimes arouse among laymen, and occasionally even among scientists, criticism relative to the disproportion between the efforts expended and the results accomplished. To what end, say the scoffers, does the chemist labor so strenuously to determine one decimal place more than his predecessors when he may fully expect to see his own measurements in turn corrected by a new generation? This reproach, which chemistry shares with all branches of metrology, arises from an inadequate appreciation of the extreme importance of certain results obtained in the course of such studies. Although less striking than the discoveries of the pioneers, who were busy with the exploration of new fields, works of a high degree of precision are not less essential to all further progress. A short review of the results obtained in science and in technical industries with the aid of this type of researches will give a better understanding of the debt due to these workers.

A. *In pure science*

(1) *Philosophy of science.* In the philosophy of science, it is just as important to define accurately the concept of species in chemistry as in biology. Clear ideas and precise notions are the prerequisites of the development of knowledge of the internal constitution of matter. There is no better example than the researches of Stas, and later those of Landolt, which demonstrated the indestructibility of matter and the constancy of the relations by weight of elements in chemical reactions.[1] Likewise, the echo of the discussions between Proust and Berthollet concerning definite compounds has not diminished since physical chemistry has placed the study of solutions in the foreground. Jaeger and Dijkstra[2] showed how beautifully the preparation of compounds of silicon in a state of perfect purity furnished a negative answer to the question of the isotopy of this element.

(2) *Pure chemistry.* Accurate measurements of the properties of imperfectly known materials have led to the discovery of numerous new substances. Cases in point are: the rare earths, caesium, thallium, etc., whose individuality was established during spectroscopic studies; the rare gases of the atmosphere discovered by Rayleigh and Ramsay[3] as a result of their determinations of the density of nitrogen; radium isolated by Madame Curie, as a result of accurate measurements of the ionizing activity of certain minerals determined readily by means of piezo-electric quartz, invented by Pierre Curie. Instances among com-

---

[1] Rutherford's sensational discoveries of atomic disintegration under the action of bombardment of particles concern facts of an entirely different order, and these in no way detract from Stas' conclusions.

[2] Jaeger & Dijkstra, Proc. Acad. Amsterdam, *27*, 393 (1924); Z. anorg. allgem. Chem., *143*, 233 (1925).

[3] Rayleigh and Ramsay, Proc. Roy. Soc., *57*, 265 (1895); Phil. Trans., *186*, 187 (1895).

pounds are: the discovery by Victor Meyer[1] of thiophene as an impurity in benzene, and the discovery of many position isomers and stereoisomers that can be differentiated with certainty only by their physical constants.

(3) *Physics.* Certain physical phenomena are exhibited only by very pure substances. For instance, the alkali earth sulfides studied by Lenard[2] show no phosphorescence unless they contain small quantities of other sulfides, with which they form solid solutions. Another example is the discovery of the super-conductivity of pure metals at temperatures of liquid helium by Kamerlingh-Onnes, a property which is masked by the secondary resistance inherent in alloys.

(4) *Metrology.* The construction of standard instruments requires a thorough knowledge of the materials employed. The (Pt-Ir) standard meter of Breteuil is made from very pure platinum, specially prepared by Stas and Ste.-Claire Deville.[3] The discovery by Guillaume[4] of invar (36% nickel steel), that has a negligible coefficient of thermal expansion, was a fruit of similar studies.

Certain very pure materials are used constantly for standardizing measuring equipment. Water and mercury are indispensable for measurements of volume, density, pressure, temperature, electrical resistance, and so on. The use of standard materials, whose constants are fixed and always reproducible, are being employed more and more in place of standard instruments that are difficult to transport and to reproduce. Sulfur, naphthalene, metals and pure salts are thus used in thermometry, atomic weight determinations, spectroscopy, calorimetry, etc.

---

[1] Meyer, Ber. *16*, 1471 (1883).

[2] Klatt and Lenard, Wied. Ann., [2] *38*, 90 (1889).

[3] Stas. Procès-verbaux du Comité des Poids et Mesures, 1880.

[4] Guillaume, Compt. rend., *124*, 176 (1897).

(5) *Stoichiometry.* This science which deals with the relationships of the structure and properties of the atom, compounds, and solutions, can advance only by virtue of increased knowledge of the true physical constants of very pure substances. For example, the regularities in atomic weights, the series in spectra, etc., are usable only if the samples being dealt with are perfectly defined.

B. *In chemical practice*

(6) *In chemical analysis.* The commercial value of many materials differs greatly according to their content of impurities (e.g. pyrites containing arsenic, ammonium nitrate contaminated with pyridine). Consequently, the accurate determination of these deleterious impurities is often the subject of disputes that can be settled only by recourse to standard analytical methods and very pure reagents. Sodium oxalate is important in this respect relative to oxidimetry, benzoic and succinic acids in acidimetry, and so on. Therefore many chemists have busied themselves with the preparation of such analytical standards. Anhydrous alcohol, the basis of all excise alcoholometry, is a typical example; pure sugar and its solutions are other instances.

(7) *In technology.* Certain industries imperatively demand products of extremely high purity. Examples are: electrolytic copper (99.99%) for conductors; catalysts free from impurities (e.g. Sabatier nickel, and platinum for the contact process must be shielded from traces of halogens, sulfur, arsenic, which poison them).

(8) *In biology and medicine.* The purity of materials used in these branches is of great importance because of the extreme sensitivity of living organisms to the action of certain impurities. For instance, water which has stood in

a nickel vessel will kill plants sprinkled with it, although the presence of the nickel cannot be detected by any known chemical reagent. The importance in anaesthesia of very pure chloroform (free of phosgene) is well known; likewise the role of pure sugars in bacteriological media. For example, typhus bacillum grown in a solution of lactose is sensitive to the presence of 0.05% glucose in the medium.[1]

Conclusions. In view of the importance acquired by the study of pure materials and their constants, as well as of the special knowledge necessary in this field, the time has come to build this collection of theories and facts into a new auxiliary science of pure chemistry. Its first aims will be to put in order the concepts concerning chemical species and to make a critical report on the methods used for the preparation of pure materials: Then will come the determination of the exact value of the constants of these substances, so that there will be available definite materials for the development of the stoichiometric study of the relations between physical properties and internal constitution of matter.

---

[1] Pfanstiehl and Black, J. Ind. Eng. Chem., *13*, 685 (1921).